PRINCIPLES OF METALLURGY

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BY

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PRINCIPLES OF METALLURGY

PREFACE.

THE Author's work on Elementary Metallurgy having
been received with considerable favour by Teachers and
Students of Metallurgy, he has been encouraged to produce
the present volume, which is an attempt to present a more
extended view of the principles of Metallurgy, including,
as far as possible, the new theories which have been
introduced in recent years.

For those who have not ready access to the Journals of
the Scientific and Industrial Societies, or the time to study
minutely the great mass of detailed information contained
therein, the abridged accounts presented in this book will,
it is hoped, be found useful.

It also aims at giving in a simple and succinct form the
views of modern Metallurgists, and the methods of pro-
cedure in the extraction of various metals from their ores,
with the uses and properties of the same when isolated.

For convenience of study and as a means of ready
reference the work is divided into a number of chapters,
where information of an allied kind is brought together.
The physical properties of the metals are considered first;
then the chemical principles involved in the various

processes are explained ; the information concerning the
Metallic Alloys is placed together ; this is succeeded by a
description of fluxes, slags, and refractory materials ; the
nature and mode of preparation of different kinds of fuel
are next referred to ; then follows a more detailed descrip-
tion of the Metallurgy of Iron and Steel, Silver, Gold,
Platinum, Lead, Copper, Zinc, Tin, Nickel, Cobalt, Alu-
minium, Antimony, Arsenic, and Bismuth.

The Author desires gratefully to acknowledge the
assistance derived from the works of Eissler, Howe,
Mendeleef, Percy, Peters, Richards, Roberts-Austen, Rose,
etc.; also from Watts' *Dictionary of Chemistry*, Thorpe's
Dictionary of Applied Chemistry, the Journals of the Iron
and Steel Institute, and various papers and articles in
the current scientific papers. He would also most thank-
fully record his deep obligation to his colleague, Mr. J.
H. Stansbie for his kindness in reading the proof sheets.

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ARTHUR H. HIORNS.

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CHAPTER I.

INTRODUCTION.

METALLURGY is that branch of Applied Science whose object
is to describe and scientifically criticise the various methods
of extracting metals from their ores, and the mode of their
application to various manufacturing purposes. It comprises
a number of physical and mechanical operations, many of
which are conducted at very high temperatures, so that a
knowledge of the principles of heat, and of the materials
capable of withstanding excessive heat, is necessary. It is,
however, in its chemical aspect that the chief part of the
subject lies, for metallurgy is essentially a chemical art, and
the student who aspires to a comprehensive knowledge of the
subject must give considerable attention to the study of the
Science of Inorganic Chemistry.

This work will comprise the following subjects:—1. General
Definitions; 2. Physical Properties of Metals; 3. Chemical
Properties of Metals; 4. Alloys; 5. Fuel; 6. Refractory
Materials and Silicates; 7. Descriptions of Metallurgical
Processes connected with the Useful Metals.

GENERAL METALLURGICAL TERMS.

Ores.—This term is used to signify those masses of metal-
liferous matter occurring in the earth from which the metals
are obtained. They are usually dressed or prepared for the
strictly metallurgical operations by the miner, before being
sent to the smelting works, so as to roughly remove the
associated earthy matter by breaking, washing, etc., and thus

reduce the bulk to the smallest desirable dimensions. The value of an ore will depend upon the nature and condition of the contained metal, and upon the elements with which it is associated. Iron ores are rarely smelted when they contain less than 30 per cent. of metal. Ores of lead and zinc are poor when they contain 30 per cent. of metal. Copper ores are very rich with 30 per cent. of copper, whilst silver and gold ores are very valuable with a few ounces of metal to the ton. The metals gold and platinum are generally found in nature in the metallic state, and silver, copper, and mercury frequently so. The metallic compounds which are most frequent as ores are :—1. Oxides, such as tin and iron oxides. Oxides are sometimes found in combination with water, such as brown hematite, sometimes with carbon dioxide, such as copper and iron carbonates. Occasionally with silica, such as zinc and lead silicates, and also with sulphur trioxide in sulphates, such as copper sulphate. 2. Sulphides ; either simple, such as galena and blende, or compound, such as copper pyrites, pyrargyrite, etc. 3. Arsenides, such as nickel and copper arsenides. The above compounds rarely occur alone, but are more or less mixed with other minerals in which they are embedded, termed vein-stuff, matrix, or gangue. These do not usually contain metals which can be profitably extracted. Such minerals are :—Quartz, carbonate of lime, and various silicates, also sulphates, fluorides, phosphates, etc. The gangue is sometimes useful in the operations in which the metal is extracted.

Smelting.—This term is applied to the process, or whole series of processes, whereby a metal or compound is separated by fusion from the ore or other material containing the metal.

Reduction.—When a metal is isolated from its state of chemical combination, it is said to be reduced, and the agent affecting the reduction is termed a reducing agent. The principal agents thus employed are carbon, carbonic oxide, hydrogen, hydrocarbons, and sometimes iron and other metals. Reduction may be partial or complete. Thus, a compound may be reduced from a higher to a lower state of combination, or completely reduced to the metallic state. For the purposes of reduction a body is generally first converted into an oxide, if not already in that form. Certain compounds of metals, such as gold, silver, and mercury, may be reduced by heat alone. Sulphides may be completely reduced by the combined action of heat and air, as is the case with the sulphides of lead and copper. When carbon is used as the reducing agent, and the oxide is easily reducible, carbon dioxide and

metal are formed ; but when the temperature required for reduction is such that carbon will reduce carbon dioxide, then carbonic oxide is produced. The reduction of oxides of copper and lead, for example, is complete even if carbon dioxide alone is formed ; but in the case of ferric oxide and zinc oxide the reduction is not complete unless carbonic oxide is present in large excess, on account of the oxidising action of carbon dioxide. Solid carbon acts but slowly as a reducing agent, but when it is united with oxygen in the form of carbonic oxide this gas rapidly penetrates to the heart of each fragment of the metallic oxide, and, absorbing its oxygen, reduces it to the metallic state. Metals, such as iron and manganese, are frequently used to remove oxygen in certain operations. Manganese plays this important part in the manufacture of steel. Iron deoxidises compounds of copper, of lead, and of mercury, and sodium acts as a reducing agent in the extraction of aluminium and magnesium from their haloid salts. Silicates of copper and nickel are reduced by the action of iron or zinc sulphides or arsenides with the formation of sulphide or arsenide of copper and nickel and silicates of iron and zinc. Sulphides may be reduced by other metals, such as the sulphides of lead and silver by iron.

Regulus and Speise.—Certain metals, such as copper and silver, possess a strong affinity for sulphur, and may be converted into sulphides by fusion with sulphur or with such bodies as iron and copper pyrites. The sulphide thus formed is termed a regulus or matt. In a similar way such metals as nickel and cobalt may be converted into arsenides by the agency of certain other arsenides. The body thus formed is termed a speise. Advantage is taken of this affinity of certain metals for sulphur and arsenic to protect them from the scorifying action of silicates during the removal of impurities.

Calcination.—This is a preliminary operation, resorted to in the case of many ores, in order to expel volatile matter, wholly or partially, by heating the substance to a temperature below its melting point, and to render it more porous and more suitable for the subsequent smelting.

Roasting.—When metalliferous matter, especially in a finely divided state, is oxidised by heating it in contact with air, or chloridised by heating with a chloride, such as common salt, it is said to be roasted. Chloridising roasting is employed for ores of gold, silver, and copper. The common salt probably acts on sulphides and sulphates at a high temperature with an exchange of chlorine for sulphur oxide, or it may be that

hydrochloric acid is formed by the action of moisture on the common salt, and then this acid acts upon the material being roasted. In the case of some sulphides it is the practice to roast them in air at a moderate temperature, so as to form sulphates, which may subsequently be dissolved out. This is the case with certain silver ores. The sulphur dioxide obtained from the roasting of ores is sometimes utilised for the manufacture of sulphuric acid. This necessitates the use of a separate chamber for the ore, so that the smoke may not come in contact with the sulphurous fumes.

Oxidising Agents.—When substances unite with oxygen they are said to be oxidised, and the body which imparts the oxygen is termed an oxidising agent. The simplest source of oxygen is atmospheric air. It contains oxygen, carbonic acid, and water vapour, all of which are oxidising agents : but by far the greater proportion consists of nitrogen, which is neutral. Water vapour readily oxidises certain metals, but in most cases it only acts in this capacity at high temperatures. The cooling effect, however, often counteracts the advantage due to oxidation. It is useful in cases where the liberated hydrogen can unite with sulphur and other impurities, while the oxygen unites with metals to form oxides, as in the roasting of sulphides and arsenides of copper. Metallic oxides, either alone or in combination with silica in basic silicates, or with sulphur in sulphates, are often employed as oxidising agents. Oxide of manganese is used in purifying iron. Basic silicate of iron acts as a carrier of oxygen in puddling and refining of iron. Oxide or sulphate of lead and sulphide of lead when heated together yield metallic lead and sulphur dioxide. Oxides and sulphides of copper or antimony act in a similar way. Carbon dioxide in the iron blast furnace oxidises iron and carbon.

Distillation and Sublimation.—When a metal or any volatile body is expelled by heat in the form of vapour, and condensed to a liquid in some cool receptacle, it is said to be distilled. Mercury and zinc are extracted from their ores by a distillation process. When the metal is condensed to a solid, as is the case with arsenic, it is then said to be sublimed.

Liquation.—In some cases one or more of the constituents of a mixture may be separated from the rest by taking advantage of their different melting points ; thus, when a mixture of lead, copper and silver is raised above the fusing point of the lead, and below that of the copper and silver, the greater part of the lead flows away, or liquates out from the unmelted copper, and carries the silver with it.

In a similar way tin is freed from iron and arsenic, sulphide of antimony and native bismuth from their associated gangues. But complete separation is never effected by this means, in consequence of the adhesion and chemical combination between the different constituents. The term liquation is also applied to the separation of any portion of a complex substance, so as to render it non-uniform, although the liquated portion may not be removed from the main mass. In many alloys, for example, when, having been melted and allowed to cool slowly, the portion which first solidifies rejects certain other portions of the constituent metals. Silver and copper, and lead and bismuth alloys are good illustrations of this property.

Scorification.—The word scoria strictly refers to the fusible compound, containing some useful metal, which is produced by the union of a suitable flux with the extraneous materials from an ore or metalliferous matter, such as silicate of lead ($2PbO . SiO_2$). When such a compound contains only earthy bases, such as lime, alumina, and magnesia, it is termed a slag or cinder ; silicate of lime and magnesia ($CaOMgOSiO_2$) will serve as an example. In this country the term slag is often used for both kinds of compounds. Scorification is the operation of converting the foreign substances present in a metallic compound into a slag or scoria by oxidation and union with silica. The vessel in which such a change is effected on the small scale is termed a scorifier. In the case of silver ores and products the impurities are oxidised by air and by lead oxide, which is easily fusible, and dissolves other oxides that may be present.

Cupellation.—This operation is performed in England in a vessel made of bone-ash, termed a "cupel," and has for its object the removal of base from noble metals by oxidation and solution in molten oxide of lead. The vessel is porous, and therefore absorbs much of the melted solution of oxides, leaving the unoxidisable metals, such as silver and gold, on the cupel. On the other hand, the German cupellation hearth is made of marl, which is largely a non-absorbent material, so that the oxide has to be removed as it is formed, being assisted in turn by the blast of air which is used for purposes of oxidation.

Amalgamation.—This, strictly speaking, is the union of mercury with other metals, but the term is also applied to the whole of the processes in which mercury is used to extract metals from their ores or products. Gold and silver, for example, are extracted from their ores, by grinding and pass-

ing over or through mercury. The amalgam is then squeezed through chamois leather, when a pasty mass containing gold or silver is left, from which the mercury is driven off by distillation.

Cementation.— When a metal is heated in contact with powdered material, such as red hematite, termed the cement, and without melting, certain of the constituents are oxidised or otherwise modified by the cement powder, and the process is termed an oxidising cementation. Cast-iron articles are in this way "annealed," as it is termed, for the production of malleable cast-iron. When a body, such as wrought-iron, is strongly heated in contact with carbon or carbonaceous matter in closed vessels, from which the air is excluded, it gradually unites with a portion of the carbon, converting the iron into steel. This is a carburising cementation. Cementation then is the reaction which takes place between two bodies, one of which is a powder, without fusion.

Metallurgical Processes.—When a metal is extracted from its ore by the assistance of a more or less high temperature, it is termed a dry process, as distinguished from the method of dissolution and precipitation of the metal in some suitable liquid, which is then termed a wet process.

Dry Processes.—Gold, silver, platinum, and copper, which occur native, are extracted by fusion, with a suitable flux, in blast or reverberatory furnaces. Mercury is reduced from its sulphide by means of heat and air, while arsenic is sublimed in a retort by the aid of heat alone.

Oxides are reduced by means of carbon; those of copper, lead, antimony, nickel, and iron in blast furnaces; those of tin and bismuth in reverberatory furnaces; those of zinc and arsenic in closed vessels; and oxide of aluminium in an electrical furnace.

Sulphides, such as those of copper and iron, are either first partially roasted to oxide and sulphate, and the products allowed to react on each other at a higher temperature in reverberatory furnaces; or the sulphide is reduced by iron; or the sulphide is roasted completely to oxide, and then reduced by carbon.

Gold and silver are often dissolved in molten lead, which has been reduced in a blast or reverberatory furnace, and finally separated by cupellation. Gold and silver are also extracted from their ores by dissolution in mercury.

Wet Processes.—In this method the metalliferous matter is first dissolved in a suitable solution, such as the common acids, common salt, chlorine water, or water alone. The

metals are usually precipitated by a cheaper metal, such as gold and silver by copper, and copper by iron. Sometimes the precipitant is a compound, such as ferrous sulphate and sulphur dioxide gas, which are employed for precipitating gold. Nickel and cobalt are precipitated as oxides, and these are reduced in the dry way.

Electro-Chemical Process.—The substance is first brought into the liquid state by fusion or by solution, and then decomposed by the passage of an electric current. The greatest success has been achieved with copper, especially in refining the crude metal. Aluminium is also extracted by electrical methods. With metals of less intrinsic value the power required is too costly, unless cheaper methods of producing electric currents than are known at present can be devised.

CHAPTER II.

PHYSICAL PROPERTIES OF METALS.

METALS are capable of existing in three forms, viz., as solids, liquids, and gases. Bodies which can support a longitudinal pressure, however small, without being supported by a lateral pressure, are called solids. A liquid differs essentially from a solid in being destitute of the power of sustaining pressure unless it is supported laterally in every direction. The distinguishing feature of a gas is that of indefinite expansion. Liquids and gases are both included under the general term of fluids. When a body is only capable of offering a small resistance to change of state, such as jelly for example, it is said to be in the colloid or semi-solid condition ; this is the case with iron at a welding temperature. Metals are generally considered to be typical solids, but their behaviour under certain circumstances proves that the difference in the two conditions is one of degree rather than of kind. A solid metal can flow like a viscous fluid if sufficient pressure is applied. This is well seen in the case of the forging of a piece of iron, in the spinning of sheet metal, in the planing and turning of metals, etc. In all these cases the material, in virtue of its plasticity, yields to the pressure, allows the molecules to slip over each other and take up new positions, so that new forms or surfaces are impressed upon them. Stamping of metals and coins, etc., is another illustration of this same property. If two pieces of lead with a coin between them be struck a sharp blow with a hammer, an impression of the coin will be formed in the lead. The lines of flow in the formation of a piece of wrought iron may be seen by polishing the surface and etching it with a solution of mercuric chloride or chromic acid.* Mr. Kreuzpointer, in discussing this subject, says the structure of a metal greatly

* *Iron Age.* Vol. XLV., p. 948.

influences the rate of flow. Steel with a distinctly granular structure flows less readily than steel with a "mushy" structure, though both may show almost identical tenacities and elongations, but as a rule the degree of ductility and elongation of a metal depends on the rate of flow of that metal.

In 1878 Professor Spring of Liege showed that the particles of a metal in the form of powder could be welded into a solid mass by great pressure. His experiments were made by the aid of a press, the form of which is shown in Fig. 1. The metallic powder is placed under a short cylinder of steel, in
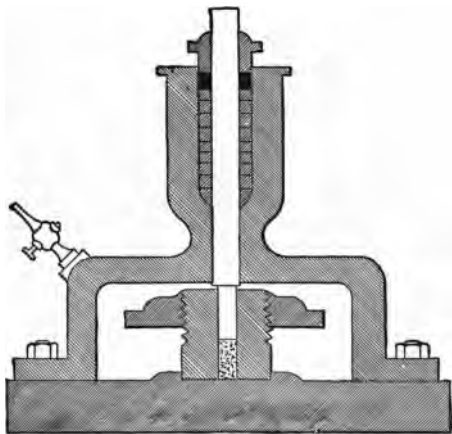
Fig. 1.

the cavity of a steel block divided vertically, held together by a collar, and placed in a chamber of gun-metal, which may be rendered vacuous. The pressure is applied to a cylindrical rod passing through a stuffing-box. Under a pressure of 2000 atmospheres or 13 tons to the square inch, lead, in the form of filings, becomes compressed to a solid block ; and under a pressure of 5000 atmospheres the metal flows through all the cracks of the apparatus like a liquid. Spring obtained some important results with crystalline metals, such as bismuth and antimony. At a pressure of 6000 atmospheres finely powdered bismuth unites into a solid mass, having a crystalline fracture. Tin when similarly compressed in powder, is made to flow through a hole

in the base forming a wire. The following table shows the amount of compression required to unite the powders of the respective metals :—

Lead	unites at 13 tons per square inch.		
Tin	,,	19	,,	,,
Zinc	,,	38	,,	,,
Antimony	,,	38	,,	,,
Aluminium	,,	38	,,	,,
Bismuth	,,	38	,,	,,
Copper	,,	33	,,	,,
Lead	flows at	33	,,	,,
Tin	,,	47	,,	,,

It occurred to Professor Spring that the particles of different metals might be united by pressure, so as to form alloys, and he considered that the formation of such alloys by pressure would afford conclusive proof that there is true union between the particles of metals in the cold, when they are brought into intimate contact. He compressed a mixture of 15 parts bismuth, 8 parts lead, 4 parts tin, and 3 parts cadmium, and produced an alloy which fuses at 100° C. It is necessary to crush up the product of the first compression, and again submit the powder to compression, in order to get a perfect alloy. The objection has been urged that the mixture may have been fused by the heat of compression. Professor Spring has experimentally proved that this was not the case. The compression was effected with extreme slowness, and he calculates that if all the work done in compressing the powders were translated into heat, it would only serve to heat a cylinder of iron 10 mm. in height and 8 mm. in diameter 40·64° C. Spring took the organic compound *phorone*, which melts at 28° C., and compressed it in precisely the same way as the metallic powders. Only imperfect union of the particles resulted, and the 28° of heat necessary to melt the phorone was not generated.

Occlusion.—The action of gases on metals is imperfectly understood, but that many metals occlude gases is well established. Hydrogen is retained by lead in secondary batteries to the extent of ·15 time the volume of the metal. Palladium, as is well known, absorbs more than 500 times its volume of hydrogen. Platinum, especially in the spongy form, is very greedy for the same gas. Gold is capable of occluding 40 to 50 times its volume of hydrogen. Silver is said by Neumann to occlude no hydrogen, but Graham states that it absorbs ·21 time its volume. Pure aluminium occludes 2·72 times its volume when in thin sheet. Iron

absorbs 19 times its volume, and copper 4½ times its
volume of hydrogen.   Nickel has a capacity for hydrogen
of about 17½ volumes.   Cobalt takes in much hydrogen,
and the metal when thus charged with hydrogen becomes
incandescent in oxygen gas.   The occlusive power of some
metals for hydrogen decreases with a repetition of the
experiments.   This is the case with the noble metals, and
is supposed to be due to an increase of density.   Iron and
cobalt act in the same way, but copper and nickel do not
decrease in occlusive power by repetition.

Silver and gold, according to Neumann, are capable of
occluding oxygen, the volumes being 4 for the former and
·48 for the latter; the amount probably varies with the
temperature.   Neumann found that platinum occludes 77·14
volumes of oxygen.   With palladium he observed the forma-
tion of a suboxide.   He considers that the absorption of
oxygen depends on the powers of the metals to become
oxidised at about 450° C., the temperature of his experi-
ments.*   Iron takes up oxygen, as in the Bessemer process,
but whether dissolved or in the form of oxide is unknown,
but Müller considers the oxygen is dissolved in the iron.

Carbonic oxide is dissolved by iron, and the simultaneous
presence of silicon and manganese appears to increase the
solvent power of the metal for carbonic oxide as well as
for hydrogen and nitrogen.

Elasticity.—This is that property of matter in virtue of
which a body requires force to change its bulk or shape, and
requires a continued application of the force to maintain the
change, and recovers its original form when the force is
removed.   If a body recovers its shape, when the force which
has caused a change of form is removed, it is termed a
perfectly elastic body.   In this sense all fluids are perfectly
elastic.   Solids, on the contrary, are generally imperfectly
elastic, but the more homogeneous the body is the more per-
fectly elastic it is likely to be.   This is the case with metals.
As a rule they will bear considerable derangement of form
and yet recover their shape; but at a certain point, varying
for each metal, and with the physical condition of the metal,
there is a limit to this alteration of form with subsequent
recovery.   This is termed the limit of elasticity.   If a metal is
impressed beyond this limit the change of form becomes
permanent, and permanent set takes place.   Within the
limit of elasticity the amount of strain produced in a metal
is proportional to the applied stress.   Beyond the limit of

* *Chemical News*, 10th March, 1893.

elasticity this proportionality ceases and the strain is much greater than before for a given stress. The load which produces this permanent set is said to be the measure of the elastic strength of a metal, for, although it may not break, it is permanently altered. If a metal could be lengthened or shortened equally by equal stresses after the limit of elasticity had been passed, there would be some stress which would stretch it to double its length or shorten it to zero. This stress, expressed in pounds per square inch of a bar of metal, is termed the Modulus of Elasticity.
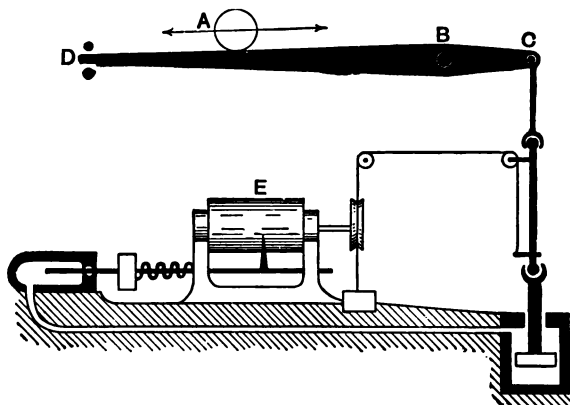
Fig. 2.

Tenacity or Tensile Strength is the power of resisting rupture by the action of a tensile stress. The molecules of different bodies are held together with varying degrees of force, and the tensile force required to effect their separation depends upon the strength with which they are held together. In determining the tensile strength of a metal the chief points to decide are : the tensile stress the metal can sustain without rupture; the limit of its elasticity and the elongation per inch on a bar one square inch of section. Sometimes it is desirable to obtain the strain within the limit of elasticity. These properties are determined by means of a testing machine. Wicksteeds' is represented diagrammatically in Fig. 2. It contains a single lever. A movable poise A measures the load, while the

pressure is applied by a ram.   The ratio of BC to BD is
50 : 1.   The poise is 1 ton, and when at D it balances 50 tons
at C.   E is a revolving drum which is actuated by the wire
attached by clips to the specimen which is being elongated.
The pencil, which is actuated by pressure of the hydraulic
press, has an axial motion proportional to the stress.   A
stress-strain diagram is thus obtained.

Testing machines have two pairs of jaws, in which the
test-piece is held, one pair being connected with the head
of the ram of a hydraulic cylinder, and the other end with
a lever carrying weights, by which the tensile stress exerted
by the hydraulic power is measured.   Some machines have
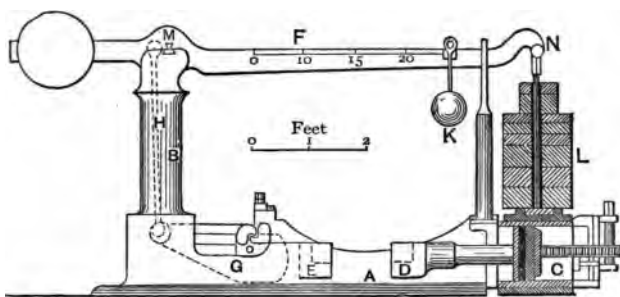
Fig. 3.
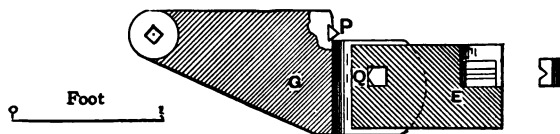
Fig. 3A.

the jaws and test-piece so arranged as to produce a pull in a
vertical plane, while in others the jaws are made to work
horizontally.

Fig. 3 represents a simple 30-ton machine, in which A
is the cast-iron bed-plate, B a hollow standard supporting
a beam or lever F at the top.   C is the hydraulic pump, the
ram of which is attached to a pair of jaws D.   The opposite
pair of jaws E are connected with the levers F and G by a
connecting rod H.   The lever F carries a jockey-weight K,

and also a rod and plate for supporting additional weights
L, which represent tons and half tons. The beam F is
supported on a knife-edge at M, the shorter arm being
balanced by a dead-weight. The distance of the knife-edge
from the point of attachment of the rod H is 2 inches, and
the length of the arm MN 56 inches, which gives a leverage
of 28 to 1. When the jockey-weight K is placed at No. 20
of the scale, it exerts a pull of 1 ton on the jaws E. The
bell-crank lever G is also supported on brackets O; it is
15 inches long, and the vertical distance from the point of
attachment to the knife-edges P is 3 inches, giving a leverage
of 5 to 1. The pull is exerted through a third knife-edge
shown at Q. Thus the total advantage gained by the com-
pound lever is $28 \times 5 = 140$; therefore a weight of 8 lbs.
suspended at L represents 1120 lbs or $\frac{1}{2}$ ton. The movable
grips or dies which hold
the test piece are shown
in Fig 3B. They are
parallel and serrated on
their inner faces, but
tapered at the back to
an incline of 1 in 6,
causing the grip to be
tightened in proportion
to the pull, and loosened when the stress is removed. The
hydraulic ram has a stroke of 8 inches.
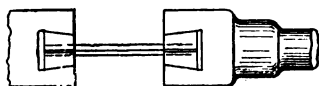
Foot

Fig. 3B.

To test a bar of iron or steel $\frac{3}{4}$ inch diameter and 8 to
12 inches long, it is placed in the grips and pressure applied
by the hydraulic pump, the jockey-weight being at zero
of the scale. A weight representing $2\frac{1}{2}$ tons is placed on
its seat, and the jockey weight gradually moved towards the
point marked 20. If this is found insufficient to balance
the pressure exerted by the pump, and the bar shows no
signs of breaking, the jockey weight is returned to zero and
an additional weight added. The above process is then
repeated, and so on until the bar breaks, when the weights
added representing tons, and the position of the jockey
weight representing fractions of a ton, are noted, the pump
being worked continuously, except during the intervals of
moving the weights. The bar is then measured, in order
to determine its amount of elongation between two marks
previously made on the bar, and its reduction of area at
the point of rupture.

In making comparative tests it is essential that all test-
pieces should be of the same length and thickness, for a thin

section will give a proportionately higher resistance per unit
of area than a thicker one. The proportional elongation
before fracture is greater with short pieces than with long
ones.

The shape and length of the test-piece, as well as the
method of holding it, also has an influence on its apparent
strength. The old method of holding specimens was by
means of pins (Fig. 4), and if the pin is sufficiently large,
and the hole exactly in the axis the plan is satisfactory,
but expensive. It is usual now to use shackles with wedge-
shaped grips for plate specimens, using test-bars as shown
in Fig 4 B. With materials which are brittle the test-bar
must be recessed, but with ductile materials it is often left
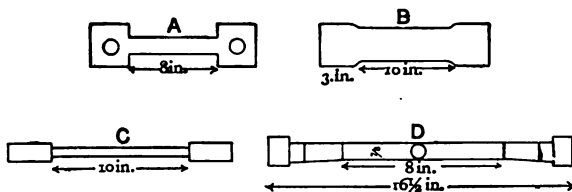
Fig. 4.

parallel; nevertheless the recessed form is best, and the
distance between the shoulders should be eight or ten
inches.

Fig. 4 c shows the form of round bars for friction grips
with V-shaped recesses, which are simple and convenient, but
the bar is liable to break at the shoulder and would be better
if made as in Fig. 4 B. The defect of a clip like this is,
that the specimen may slip a little on the one side, being
held less tightly than on the other; the specimen then
breaks by tearing. Many specimens are prepared with a
screw-thread chased on the ends, on which nuts are screwed,
these being held in a clip; this plan is expensive, and is
objectionable if the screw-threads are not accurate. Professor
Unwin considers the official German test-bar (Fig. 4 D) the
best form of specimen for tension experiments. The test-
bar is formed with collars, under which are placed two
halves of a ring having a spherical bearing-surface, the only
objection being its expense.

Professor Dewar * has shown that all the common metals
and alloys increase in tenacity at low temperatures, thus

* *Chemical News*, 26th April, 1895.

the tenacity of iron is nearly double at ‑200° C. to what it is
at 15° C. ; the following tables show his results :—

Breaking Stress in lbs. of Wires ·098 inch diameter.			Breaking Stress in lbs. Cast Rods ·2 inch diameter.		
	15° c.	– 182° c.		15° c.	– 182° c.
Steel, . .	420	700	Tin, . .	200	390
Iron, . .	320	670	Lead, . .	77	170
Copper, . .	200	300	Zinc, . .	35	26
Brass, . .	310	440	Mercury, .	—	31
German Silver,	470	600	Bismuth, .	60	30
Gold, . .	255	340	Antimony, .	61	30
Silver, . .	330	420	Solder, . .	300	645
			Wood's Alloy,	140	450

The diminished strength in zinc, bismuth, and antimony
is probably due to strains produced in cooling such highly
crystalline metals.

TOUGHNESS is the property of resisting fracture by bending,
torsion, etc., after the limit of elasticity has been reached, as
seen in the case of the metals copper and lead.

MALLEABILITY.—When a body can be permanently flattened
in all directions by hammering or rolling without cracking
it is said to be malleable.   The malleability of a metal
depends on its softness and on its tenacity.   Crystalline
metals are not generally malleable, but brittle, and there-
fore any impurity or mechanical action which induces a
crystalline structure in a metal will affect its malleability.
During the working of metals their molecules are forced
into unnatural positions, but by annealing they are largely
restored to a normal state.   Gold is the most malleable of
the metals, combining the two properties of softness and
tenacity in the highest degree.   In some metals an increase
of temperature increases the *malleability*, while in others the
reverse occurs.   Commercial zinc is peculiar, being brittle
when cold and when hot, but at temperatures between 100°
and 200° C. it is malleable.   The presence of foreign elements
very often alters the malleability of a metal ; thus, iron
containing a little sulphur is brittle when hot but malleable
when cold.   On the other hand a little phosphorus acts on
iron in the opposite manner.   It is then said to be hot-short
and cold-short respectively.   The relative malleability of
metals is determined by the degree of thinness to which they
may be reduced from the same thickness without annealing.

DUCTILITY.—When a metal is capable of being drawn into wire, or lengthened by a tensile force, combined with lateral compression, without breaking, it is said to be ductile. The ease with which it may be reduced will depend on its softness, but the thinness to which it may be drawn will depend on its tenacity. The rate at which the traction is applied also exerts an influence on this property. The following metals are arranged in the order of their malleability and ductility.

Malleability.—Gold, silver, copper, tin, platinum, lead, zinc, iron, nickel.

Ductility.—Gold, silver, platinum, iron, nickel, copper, zinc, tin, lead.

Specific Gravity, or Specific Density, is the number which expresses the weight of a body compared with that of an equal bulk of water, which is taken as unity. The processes of hammering, rolling, stamping, etc., tend to increase the specific gravities of all malleable metals by closing any pores. The density of a metal therefore depends on the compactness of its structure. With the exception of bismuth, all metals are denser in the solid than in the liquid state. If a metal is free from cavities no amount of compression can increase its density, unless the effect of the compression is such as to cause a molecular rearrangement. The specific gravities of the following metals are : Platinum, 21·5 ; gold, 19·3 ; mercury, 13·59 ; lead, 11·40 ; silver, 10·50 ; bismuth, 9·80 ; copper, 8·82 ; nickel, 8·80 ; manganese, 8·00 ; iron, 7·90 ; tin, 7·29 ; zinc, 7·10 ; antimony, 6·70 ; arsenic, 5·67 ; aluminium, 2·56 ; magnesium, 1·74 ; sodium, ·97 ; potassium, ·87 ; lithium, ·58.

| | Specific Gravity of Solid. | FLUID DENSITY. | | Percentage of Change in Volume from Cold Solid to Liquid. |
		By Mallet's Method.	By Oncosi-meter.	
Bismuth, .	9·82	10·039	10·055	Decrease of volume 2·30
Copper, .	8·80	—	8·217	Increase of volume 7·10
Lead, .	11·40	10·650	10·370	,, ,, 9·93
Tin, .	7·50	6·974	7·025	,, ,, 6·76
Zinc, .	7·20	6·550	6·480	,, ,, 11·10
Silver, .	10·57	9·460	9·510	,, ,, 11·20
Iron (No. 4 foundry pig),	6·95	—	6·880	,, ,, 1·02
Iron, cast, (mixed brands	7·17	6·650	—	

B

The fluid densities of several metals by means of the oncosimeter* have been determined by Wrightson and Roberts-Austen, and their results are summarised in the preceding table.

Specific Heat is the number which expresses the capacity for heat which a body possesses compared with that possessed by an equal weight of water. Different metals require different amounts of heat to raise equal weights from 0° to 1° C.

TABLE OF SPECIFIC HEATS OF METALS.							
Iron,	.	.	.	·110	Tin,	.	.	.	·056
Nickel,	.	.	.	·110	Antimony,	.	.	·051
Zinc,	.	.	.	·094	Platinum,.	.	.	·033
Copper,	.	.	.	·094	Gold,	.	.	.	·032
Silver,	.	.	.	·056	Lead,	.	.	.	·031

Hardness, or resistance to abrasion or cutting, is generally increased by the presence of impurities in a metal, so that softness in many cases is a test of purity. The softness increases with increase of temperature. Manganese, cobalt, and nickel are the hardest, and lead the softest of the metals considered in this work. Metals that possess high limits of elasticity are usually very hard. Hardness depends on the attraction of the molecules for each other.

Brittleness.—When a metal readily breaks into fragments by the occurrence of a sudden shock, or if a metal is unable to resist fracture when subjected to a compressive or percussive force, as in the case of rolling and hammering, it is termed brittle. Impurities generally increase the brittleness. Brittleness is not hardness, as sealing wax, for example, is brittle but not hard. A substance is brittle when it does not exhibit elongation, but if it cannot be scratched with glass or quartz it is hard. If a metal is crystalline, and the cohesion between the crystals is feeble, then the metal is brittle.

Odour and Taste.—Many metals when rubbed or raised in temperature emit a characteristic odour, and when applied to the tongue produce a peculiar taste, even when chemically pure.

* *Journal of Iron and Steel Institute*, 1880.

Sonorousness. — This property is possessed by the harder metals, and is very marked in certain alloys, such as those of copper and tin. Lead becomes sonorous when cast in the form of a mushroom. Impurities sometimes increase the sonorousness of a metal, as is the case with antimony in lead. Aluminium emits a clear sound when struck. Bar tin yields a crackling sound when bent, and is supposed to be due to the sliding of the crystals over each other.

Conductivity is the power different bodies possess of transmitting heat and electricity. The conducting power for heat is about the same as that for electricity, and a very small quantity of impurity in a metal will often seriously affect its conductivity. ·5 per cent. of iron in copper will reduce its conductivity 50 per cent., and a much smaller quantity will render it unfit for many electrical purposes. The conducting power of metals is diminished by a rise in temperature, and in metals which undergo no molecular change before fusion, the increase of electrical resistance is proportional to the temperature. The following is the probable order of conductivity : Silver, copper, gold, tin, iron, nickel, lead, platinum, antimony, bismuth. Profs. Dewar and Jenkin determined the conductivity of metals and alloys at very low temperatures, and found that the resistances of pure metals decrease in such a manner as to convey the idea that if the absolute zero could be obtained the resistance would vanish. The electrical resistances of alloys do not diminish in the same manner. Thus at −200° C. the alloys platinoid, german silver, platinum silver, and phosphor bronze show nearly the same resistance as at 0° C.

Varieties of Fracture.—The character of the fractured surface of a metal often affords a general guide as to its properties and adaptability for various uses. Any condition that affects the cohesion or molecular condition of a metal alters its fracture. Zinc, antimony, spiegeleisen, etc., are crystalline ; grey pig-iron, steel, and bronze are granular ; copper is finely granular and silky ; wrought-iron and nickel are fibrous ; tin, if allowed to fall some distance when on the point of melting, assumes a columnar structure ; also lead and other metals, broken when very hot, act in a similar way ; certain brittle alloys, as well as hardened steel, break, like glass, with a conchoidal fracture.

Crystallisation. —Certain brittle metals, such as zinc, antimony, and bismuth, exhibit a well-defined crystalline

structure on their fractured surfaces ; also malleable metals,
such as tin, readily assume a crystalline form under certain
circumstances. Most metals appear to crystallise either in
the rhombohedral system, such as bismuth and spiegel-eisen,
or in the cubic system, chiefly in the latter. This is the
case with platinum, silver, gold, copper, lead, and iron,
and probably with tin and zinc. Tin also crystallises in
the tetragonal system. Zinc also crystallises in the hexa-
gonal system like antimony and arsenic. Tin and zinc
are therefore dimorphous. In some instances a crystalline
structure is induced by vibration, prolonged hammering,
or by intense cold, as in the case of iron and brass. Some
combinations, containing different elements, may have one
or more constituents separated from the rest by crystal-
lisation, such as graphite from cast-iron, lead and silver
from argentiferous lead, zinc and silver from lead, etc.
Metals may crystallise (1) on solidification after fusion ;
(2) by condensation from a state of vapour ; (3) by electro-
lytic deposition, as in the case of copper when a weak
current is employed.

Influence of Heat.—The following table gives the
approximate melting points of various metals :

Platinum,	.	.	1775°	Aluminium,	.	.	625°
Iron,	.	.	.	1600°	Antimony,	.	.	440°
Nickel,	.	.	about 1600°	Zinc,	.	.	415°
Grey pig-iron,	about 1250°	Lead,	.	.	325°
White pig-iron,	about 1150°	Cadmium,	.	.	320°
Steel,	less than iron but	Bismuth,	.	.	268°
	above that of pig-iron.	Tin,	.	.	227° γ^3
Copper,	.	.	.	1050°	Lithium,	.	.	180°
Gold,	.	.	.	1045°	Sodium,	.	.	95°
Silver,	.	.	.	945°	Potassium,	.	.	62°
Magnesium,	.	.	750°	Mercury,	.	.	−39°

Thus tin, lead, and zinc melt below a red heat ; aluminium
requires a red heat ; gold, silver, and copper require a bright
red heat ; iron and nickel require an intense white heat ;
while platinum only melts at the temperature of the electric
arc, or that of the oxy-hydrogen flame. Some metals, such
as antimony and zinc, readily vaporise when heated much
above their melting points, and arsenic is so volatile that
it passes when heated directly from the solid to the gaseous
state without liquefying. If, however, it be heated under
great pressure liquefaction occurs. No metal can be said
to be absolutely "fixed," as all metals can be volatilised if
raised to a sufficiently high temperature. The following

table by Pouillet will give a general idea of the temperature corresponding to different colours, although the numbers are rather too high :

Incipient red heat corresponds to		.		.	525° C.	977° F.
Dull red	.	.	.	.	700	1292
Incipient cherry red	.	.			800	1472
Cherry red	.	.	.		900	1652
Clear cherry red	.	.	.		1000	1832
Deep orange	.	.			1100	2012
Clear orange	.	.			1200	2192
White	.	.		.	1300	2372
Bright white	.	.		.	1400	2552
Dazzling white	.		.	.	1500	2732

Metals expand when heated and contract on cooling, and within certain limits the expansion is proportional to the degree of heat. Certain anomalies, however, exist, thus: cast-iron expands at the moment of becoming solid, and bismuth occupies more space in the solid than in the liquid state.

Welding.—When two pieces of metal are joined together by pressure to form one compact piece, they are said to be welded. It is necessary that the metals should be soft, with clean surfaces, and that they should possess considerable malleability and toughness. The requisite conditions for welding iron are only obtained at a high temperature, when the metal is in a pasty state. The motion of the molecules at a high temperature is raised to such a degree that they are capable of interpenetrating or diffusing into each other. Steel requires to be welded at a much lower temperature than iron, because of its lower melting point, and because the carbon is more likely to burn off if the heat be too intense ; this is the reason why it is so difficult to weld hard steel to iron. If the ends of a newly fractured bar of steel are placed together, and the broken part covered with a sheet of platinum foil, so as to exclude the air, the two parts will unite by simply heating the junction with a Bunsen burner to a low red heat, and without any pressure being applied. Such a weld, of course, can be easily broken.

Forging.—When a metal is capable of being hammered out into various shapes, the operation is termed forging. This property is the same as that of malleability, but has a more limited meaning. Forging is an illustration of the solid flow of metals.

SOLDERING.—This name is applied to the operation of joining two surfaces of a metal or metals together by heat. In

the Richemont process of lead burning, as it is termed, two pieces of lead are fused together at the edges by means of the oxy-hydrogen blow-pipe, as in some cases the introduction of solder would not be admissible. This is the case with the sheet lead lining of acid chambers. Solders are divided into two classes—hard and soft, or difficultly and easily fusible. When a red heat is required to melt the solder, the operation is termed brazing. Brass solder belongs to this class. The solder must in all cases have a lower melting point than the metals to be soldered.

Micro-structure.—The prominence given to the microscopical examination of metals is mainly owing to the facts communicated by Dr. Sorby more than thirty years ago, and since that time this method of investigation has been taken up by numerous other workers, more especially in relation to the metallurgy of iron and steel. Among other workers in microscopy as applied to metals may be mentioned the names of Osmond, Martens, Wedding, and Arnold. As metals cannot be obtained in sufficiently transparent sections, they have to be viewed by reflected light. For this purpose it is essential that they should be perfectly smooth, which is effected by grinding and polishing. Dr. Sorby's method of preparing sections consists of cutting slices about $\frac{1}{10}$ of an inch thick, and fixing them on to a glass plate by means of Canada balsam. The upper surface is first ground by rubbing on emery paper, and finishing on the very finest quality of emery paper. The surface is next rubbed on Water-of-Ayr stone until all scratches are removed. It is then polished on wet cloth stretched on a piece of wood, using, in the first place, the finest grained crocus, and, lastly, the finest rouge, so as to give a high degree of polish. Some of Dr. Sorby's specimens were polished dry on parchment covered with rouge. When the polishing is complete the surface is etched with very dilute nitric acid, in which it is plunged for a few seconds, then swilled in hot water and examined under the microscope. If the etching has not been sufficient, the acid treatment is repeated. Instead of nitric acid, a mixture of equal parts of sulphuric acid and potassium bichromate in ten times their amount of water, may be used.*

For the examination of the specimens prepared as above it is advisable to fix an illuminator in the axis of the microscope. Beck of London has introduced a vertical illuminator which can be fixed to the bottom of the tube. It consists of a circular disc of glass capable of rotation in a vertical plane,

* See *Journal of Iron and Steel Institute*, No. 1, p. 294, 1894.

and it can be so fixed as to receive the light from a lamp placed opposite a hole in the case in which a mirror is mounted. The mirror is placed at such an angle as to reflect
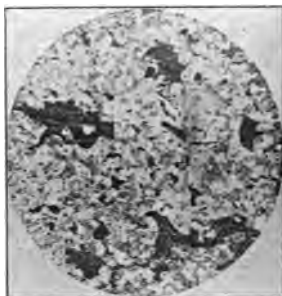
Fig. 5.

the light on to the object, and this in turn reflects the light directly through the centre of the transparent mirror to the eye-piece. Methods of oblique illumination are also used, but the simple method described above is probably as good as any.

Fig. 6.

From the microscopic study of iron it appears to be constituted, like crystalline minerals, of different bodies which have different crystallising temperatures. Take the case of the meteoric iron * (Fig. 10). It appears to contain three

* See *Journal of Iron and Steel Institute*, No. 1, 1887.

separate components. The dominant constituent seems to have crystallised first in strongly marked thin meshes; between these meshes the second constituent has crystallised.

Fig. 7.
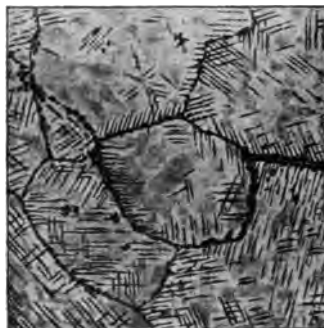
Fig. 8.

The third constituent, which is a phosphide of iron and nickel, occupies a position between the other two.

Howe has proposed names for the crystallised bodies of
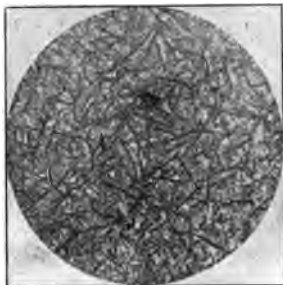
Fig. 9.

Fig. 10.

which iron and steel appear to be made up when viewed through the microscope. Thus, in Fig. 5, the iron, independent of the black patches of slag, is of nearly uniform character, to which he has given the name of *ferrite*. It

consists of imperfectly crystallised grains. The same body is seen in Fig. 6; and in Fig. 8 ferrite is indicated by dark parallel plates. Fig. 7 is a specimen of blister steel. It consists almost entirely of crystals of an intensely hard compound of iron and carbon, which has been termed *Cementite*. It is abundant in soft steel. *Pearlite* is assumed to be made up of ferrite and cementite, and contains from ·6 to 1·5 of carbon. Moderately hard steels consist largely of pearlite. The Bessemer steel, Fig. 8, is chiefly made up of pearlite. The dark portions are iron, probably free from carbon, and were rejected when the pearlite crystallised. *Hardenite* is another constituent of steel containing iron and up to 3 per cent. of hardening carbon. Fig. 9 represents a sample of grey pig-iron, containing large plates of graphite, mixed with portions of iron free from combined carbon and pearlite. Sorby assumes that the graphite crystallises first, setting free some iron ; then the pearlite crystallises out, throwing off an impure residue.

CHAPTER III.

CHEMICAL PRINCIPLES.

THE science of chemistry is built upon the great conception that matter is indestructible ; it can neither be created nor destroyed. In all experiments hitherto made it has never been observed that the weights of the substances employed are greater or less than the substances formed. Iron rusts in damp air, and most metals undergo a similar change if the temperature is sufficiently high ; and if they are accurately weighed before and after the experiment, they will be found to be heavier in the latter case, because they have absorbed something from the air. The old alchemists and early chemists supposed that rust was the simpler body, and that the metal had lost something in the act of rusting ; this they called phlogiston. If an oxide, such as mercury oxide, be sufficiently heated it will be decomposed, with the liberation of oxygen gas and the separation of the metal. In this case the metal was supposed to have gained phlogiston. In the absence of any law, the alchemists performed a number of experiments in an empirical manner, and thus accumulated a series of facts ready for explanation. Take the natural mineral galena, for example. By heat they extracted lead from it, and by further heating in a suitable vessel they finally obtained silver ; what more natural than to suppose that the metallic looking mineral had been transmuted first into lead, then into silver. From these and other facts the idea of the infinite transmutability of matter originated. Having got silver from lead, they aimed at getting gold from silver, diamonds from stones, perpetual youth from a certain drug or stone. Had they weighed the substances, they would have discovered that the lead weighs much less than the galena, and the silver incomparably less than the lead.

The above experiments with regard to rusting of metals and the separation of the constituents of the rust are now termed oxidation and reduction. With respect to the latter, the change is seldom effected by heat in the simple way mentioned for mercury oxide, but carbon or some other body is required to unite with the oxygen before it can be removed from the metal. These two great classes of chemical change were explained by the theory of phlogiston. The more oxidisable or combustible a body is, the richer it was said to be in phlogiston ; hence carbon contained it in great abundance, and by reducing earthy substances (oxides) it imparted to the reduced metals some of its phlogiston. This theory was refuted by the great French chemist Lavoisier, who proved that in every case of oxidation by heating in air the increase in weight came from the atmosphere. The fact that the weight of the oxide formed was greater than that of the metal was known to Stahl and others, but he assumed that phlogiston was lighter than air and so decreased the weight of the substance to which it was added. The classic researches of Lavoisier started a new epoch in chemistry, and formed the foundation of the science as we now know it. The great majority of substances have been found to be of a compound nature, and only a very small number to be undecomposable, and termed elements. Moreover, no chemist has been able to transmute one element into another, and no fact has been discovered which would lead one to suppose that such a transformation is possible.

All homogeneous substances are either simple or compound. Simple matter or elements do not decompose by heat or electricity, and, from their spectra, even in the sun, we must conclude that the most intense temperature is unable to change them. It has been found convenient to represent each element by the initial letter of its Latin name, and where two elements begin with the same letter, a small letter is added to distinguish one from the other. A compound is represented by a combination of the symbols of the elements of which it is composed. The symbol of an element also expresses a definite relative weight, which is assumed to be the weight of the atom, and termed *atomic weight*. Elements therefore exist alone and in combination, but we cannot say in what state an element may exist, or that its condition is the same in combination as it is when free. The only certain unalterable quality we know of is its weight. Thus, if the formula for lead oxide is PbO, we cannot deny that it consists of solid lead and gaseous oxygen;

but what we can say is that for every 207 parts by weigh
of lead there are 16 parts by weight of oxygen.   If a
element has, in any notable degree, the physical propertie
which are such prominent features of gold, viz., a peculia
lustre, opacity, great conductivity for heat and electricit;
and, to a certain extent, high specific gravity, we call it
metal. Other elements are termed non-metals. The follow
ing table gives the symbols, atomic weights, etc., of th
elements :

<div align="center">METALS.</div>

Names.	Symbols.	Atomic Weights.	Specific Gravity.
Aluminium, . . .	Al	27	2·56
Antimony, . . .	Sb	120	6·72
Arsenic, . . .	As	75	5·67
Barium, . . .	Ba	137	3·75
Bismuth, . . .	Bi	207·5	9·8
Cadmium, . . .	Cd	112	8·6
Cæsium, . . .	Cs	133	1·88
Calcium, . . .	Ca	40	1·58
Cerium, . . .	Ce	141	6·68
Chromium, . . .	Cr	52·4	6·8
Cobalt, . . .	Co	58·6	8·5
Copper, . . .	Cu	63·2	8·8
Didymium, . . .	Di	145	6·5
Erbium, . . .	E	112·6	—
Glucinum, . . .	Gl	9	2
Gold, . . .	Au	196·2	19·32
Indium, . . .	In	113·4	7·4
Iridium, . . .	Ir	192·5	22·4
Iron, . . .	Fe	56	7·86
Lanthanium, . . .	La	138·5	6·2
Lead, . . .	Pb	206·4	11·37
Lithium, . . .	Li	7	·58
Magnesium, . . .	Mg	24	1·74
Manganese, . . .	Mn	55	8
Mercury, . . .	Hg	200	13·59
Molybdenum, . . .	Mo	96	8·6
Nickel, . . .	Ni	58·6	8·8
Niobium, . . .	Nb	94	6·27
Osmium, . . .	Os	195	22·48
Palladium, . . .	Pd	106·2	11·5
Platinum, . . .	Pt	194·3	21·5
Potassium, . . .	K	39·1	·87
Rhodium, . . .	Rh	104	12·1
Rubidium, . . .	Rb	85·2	1·52
Ruthenium, . . .	Ru	103·5	12·26
Silver, . . .	Ag	107·7	10·5

METALS—*Continued.*

Names.	Symbols.	Atomic Weights.	Specific Gravity.
Sodium, . . .	Na	23	·97
Strontium, . . .	Sr	87·2	2·54
Tantalum, . . .	Ta	182	10·8
Tellurium, . . .	Te	126·3	6·25
Thallium, . . .	Tl	203·5	11·9
Thorium, . . .	Th	232	11·1
Tin, ...	Sn	117·4	7·3
Titanium, . . .	Ti	48	—
Tungsten, . . .	W	184	19·1
Uranium, . . .	U	240	18·7
Vanadium, . . .	V	51	5·5
Yttrium, . . .	Y	61·7	—
Zinc, . . .	Zn	65	7·15
Zirconium, . . .	Zr	90·4	4·15

NON-METALS.

Names.	Symbols.	Atomic Weights.	Specific Gravity.
Boron, ...	B	11	2·68
Bromine, . . .	Br	80	2·96
Carbon { Graphite, . .	—	—	2·2
Carbon { Graphite	C	12	—
Carbon { Diamond, . .	—	—	3·5
Chlorine, . . .	Cl	35·5	—
Fluorine, . . .	F	19	—
Hydrogen ? . . .	H	1	—
Iodine, . . .	I	127	4·95
Nitrogen, . . .	N	14	—
Oxygen, . . .	O	16	—
Phosphorus, . . .	P	31	1·8–2·1
Selenium, . . .	Se	79·5	4·28–4·8
Silicon, . . .	Si	28·1	2·49
Sulphur, . . .	S	32	1·97–2·07
Tellurium, . . .	Te	126·3	6·25

There are several systems of nomenclature, but the simplest for compounds containing two elements is that of writing the name of the metal first and that of the non-metal or least metallic element afterwards, giving it the termination "ide." When two non-metals combine, the one which is most unlike a metal is written second. Sometimes Greek prefixes are used for the element of the second position, such

as mono, di, tri, tetr, etc., to indicate the number of atoms present. Another system is to make the metal terminate in "ic" or "ous." That compound which contains the greater proportion of the non-metallic constituent is distinguished by the suffix "ic" and that containing the lesser by "ous." The following list will illustrate these points.

Name.	Name.	Name.	Formula.
Iron oxide,	Ferrous oxide,	Iron protoxide,	$FeO.$
Iron trioxide,	Ferric oxide,	Iron sesquioxide,	$Fe_2O_3.$
Iron tetroxide,	Triferric tetroxide,	Black oxide of iron,	$Fe_3O_4.$
Manganese oxide,	Manganous oxide,	Manganese protoxide, }	$MnO.$
Manganese dioxide	Black oxide of Manganese, }	Manganese peroxide, }	$MnO_2.$
Aluminium oxide,	Alumina,	—	$Al_2O_3.$
Calcium oxide,	Lime,	—	$CaO.$
Magnesium oxide,	Magnesia,	—	$MgO.$
Titanium oxide,	Titanic acid,	—	$TiO_2.$
Carbon monoxide,	Carbonic oxide,	—	$CO.$
Carbon dioxide,	Carbonic acid,	—	$CO_2.$
Silicon dioxide,	Silica,	—	$SiO_2.$
Phosphorus pentoxide, }	Phosphoric acid,	—	$P_2O_5.$
Sulphur dioxide,	Sulphurous acid,	—	$SO_2.$
Sulphur trioxide,	Sulphuric acid,	—	$SO_3.$

When three or more elements—one being a metal and the other oxygen—are combined together, the name of the second is made to end in "ate." In the following list a few compounds are given to illustrate this, but it should be observed that the order of placing the symbols is immaterial. In works on metallurgy the arrangement of formulæ in the last column is the more common.

Name.	Name.	Formulæ.
Iron silicate,	Ferrous silicate,	$FeSiO_3$ or $FeO.SiO_2.$
" "	" "	Fe_2SiO_4 or $2FeO.SiO_2.$
Iron sulphate,	Ferrous sulphate,	$FeSO_4$ or $FeO.SO_3.$
Calcium silicate,	Silicate of lime,	$CaSiO_3$ or $CaO.SiO_2.$
Aluminium silicate,	Silicate of alumina,	$Al_4Si_3O_{12}$ or $2Al_2O_3.3SiO_2.$
Calcium carbonate,	Limestone,	$CaCO_3$ or $CaO.CO_2.$
Iron carbonate,	Ferrous carbonate,	$FeCO_3$ or $FeO.CO_2.$

Equations.—When two or more elements unite to form a compound, or two compounds unite to form a more complex compound, the change may be represented by a chemical equation, thus :—

$$3Fe + 4O = Fe_3O_4.$$
Iron.   Oxygen.   Iron tetroxide.

$$FeO + SiO_2 = FeO.SiO_2.$$
Ferrous oxide.   Silica.   Ferrous silicate.
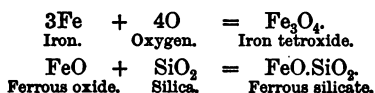
Any chemical change may be so represented, the bodies taking part in the change being placed on the left hand side of the sign of equality " $=$," and the bodies formed after the change, on the right hand side.

The quantities involved in any such change can be seen at a glance, since the symbol of an element represents a definite weight, given in the table, p. 28, as the atomic or combining weight. Thus, in the first equation 3×56 parts of iron unite with 4×16 parts of oxygen to form $168 + 64 = 232$ parts of the black oxide of iron.

When substances combine with oxygen they are said to be "oxidised," and the substance which imparts the oxygen is termed an oxidising agent. Conversely, substances which remove oxygen from a body are termed reducing agents. The following list gives some examples of both kinds.

Oxidising Agents.
Oxygen (O).
Air (O and N).
Iron tetroxide (Fe_3O_4).
Iron trioxide (Fe_2O_3).
Slags containing the above or similar oxides.
Carbon dioxide (CO_2).
Water (H_2O).

Reducing Agents.
Carbon (C).
Carbonic oxide (CO).
Hydrogen (H).
Compounds of carbon and hydrogen, such as coal gas.
Sometimes metals.

Examples of Oxidation.

$$3FeO + O = Fe_3O_4.$$
Ferrous oxide.   Oxygen.   Iron tetroxide.

$$2(2FeO.SiO_2) + O = Fe_2O_3 + 2(FeO.SiO_2).$$
Tap cinder.   Oxygen.   Ferric oxide.   Iron silicate.

$$3FeCO_3 + O = Fe_3O_4 + 3CO_2.$$
Iron carbonate.   Oxygen.   Iron tetroxide.   Carbonic acid.

$$3FeO + CO_2 = Fe_3O_4 + CO.$$
Ferrous oxide.   Carbon dioxide.   Iron tetroxide.   Carbonic oxide.

Examples of Reduction.

$$Fe_2O_3 \; + \; 6H \; = \; 2Fe \; + \; 3H_2O.$$
Ferric oxide.   Hydrogen.   Iron.   Water.

$$Fe_2O_3 \; + \; 3C \; = \; 2Fe \; + \; 3CO.$$
Ferric oxide.   Carbon.   Iron.   Carbonic oxide

$$Fe_2O_3 \; + \; 3CO \; = \; 2Fe \; + \; 3CO_2.$$
Ferric oxide.   Carbonic oxide.   Iron.   Carbonic acid.

$$PbS \; + \; Fe \; = \; FeS \; + \; Pb.$$
Lead sulphide.   Iron.   Iron sulphide.   Lead.

It will be obvious that in the cases of oxidation and re-duction the change may be partial or complete. Thus, iron is completely oxidised when converted into Fe_2O_3, and oxide of iron is completely reduced when it is all brought to the metallic state.

The following is a short description of the chief substances mentioned in the present chapter and which are subsequently alluded to.

Oxygen (O).—This is the most abundant element, form-ing probably one half the solid mass of the earth, ⅝ths of all water, and about 21 per cent. by volume of the air. It is necessary for life and all ordinary processes of combustion. In the air it is a gas, but in its compounds it is chiefly a solid or a liquid. Its oxidising action has been already mentioned. It is the chief supporter of combustion, that is, it forms the active medium in which bodies burn.

Oxides, as the compounds of oxygen with other elements are termed, are divided into two groups :—1. Those which have an acid character, chiefly oxides of the non-metals, and often termed acids, such as CO_2 and SiO_2. 2. Those of a basic character, chiefly oxides of the metals, which are termed bases. These two classes are opposite in character, and when united in equivalent proportions, they neutralise each other, forming what are termed "neutral" bodies, which do not possess the characteristic properties of either kind. Thus silica (SiO_2) will neutralise oxide of iron (FeO), forming a silicate which is neither acid nor basic. If any compound contain an excess of acid or base, it is classified either as an acid or as a basic substance according to the kind which pre-dominates. Thus, $3FeO.SiO_2$ is a basic silicate, and $FeO.SiO_2$ an acid silicate, because in the former there is more FeO than is required to neutralise the acid SiO_2, and in the latter less than is necessary for this purpose.

Hydrogen (H) is chiefly found in nature in combination with oxygen, forming water (H₂O), which contains ⅑th its weight of hydrogen. It differs from other non-metals in not generally uniting with metals to form compounds, but metals such as palladium and iron absorb it in large quantities, when it is said to be occluded. It burns in air or in pure oxygen, forming water and evolving great heat. It is a constituent of wood, peat, and coal, in which it probably exists as water, and coal-gas, and in combination with carbon it forms what are termed hydrocarbons, such as marsh gas (CH₄) and olefiant gas (C₂H₄). When the latter are burnt the hydrogen forms water, thus :

$$CH_4 \ + \ 4O \ = \ CO_2 \ + \ 2H_2O.$$
Marsh gas. Oxygen. Carbon dioxide. Water.
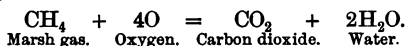
The heat produced by its combustion is in some cases more than neutralised by the great amount of heat absorbed by the water. In some furnaces and gas producers, steam is introduced along with air to increase the volume of combustible gases, but for the reason stated above, only a very limited amount of steam can be used for this purpose. On account of the readiness of hydrogen to unite with oxygen it is used as a reducing agent, and thus removes the oxygen from a compound containing it.

Nitrogen (N) forms about 79 per cent. by volume of the air, its chief function being to modify the active properties of oxygen. It neither burns nor supports combustion, so that the nitrogen which enters a furnace, for the most part, comes out unchanged, thus robbing it of a large amount of heat without contributing any itself.

Air is chiefly a mixture of oxygen and nitrogen along with small quantities of water and carbon dioxide. Omitting the latter, its composition may be taken as :

	By volume.	By weight.
N	79	77
O	21	23
	100	100

A ton of air thus contains about 515 lbs. of oxygen. It resembles oxygen in its properties, but is less active on account of the inactive nitrogen.

Silicon (Si).—This non-metal is a greyish black substance. It is generally present in iron, and supposed to exist like carbon in the "free" and in the "combined" state. It is of little importance as an element, but in combination

C

it forms about $\frac{1}{5}$th of the earth's crust. It burns in oxygen, forming silica, thus :

$$\underset{\text{Silicon.}}{\text{Si}} + \underset{\text{Oxygen.}}{2\text{O}} = \underset{\text{Silica.}}{\text{SiO}_2.}$$

Silica (SiO_2) plays a prominent part in the reduction of metals from their ores—being the chief slag-forming substance. It exists largely as sand, and in combination with "bases" termed silicates. The various slags produced in metallurgical operations are combinations of (SiO_2) with alumina (Al_2O_3), lime (CaO), ferrous oxide (FeO), manganese oxide (MnO), etc., and fuse at high temperatures. Uncombined silica is practically infusible.

Carbon (C).—This non-metal is an essential constituent of all living matter and of all ordinary fuels such as coal. It exists in the free state as the diamond, and as graphite or black-lead. In the latter form it is used in the manufacture of crucibles, etc., because of its infusibility and its non-tendency to form fusible slags with acid or basic substances: it will burn away in contact with air, but will not melt or vaporise. It exists in pig iron and steel in the free and in the combined state. Part of the free carbon of pig iron sometimes rises to the surface of the molten mass, when allowed to stand, and is known as "kish." Charcoal and coke are almost entirely composed of carbon with a little earthy matter which is left as ash when the carbon is burnt. Either form of carbon will burn in oxygen, forming oxides. When carbon is strongly heated in the presence of steam the latter is decomposed and the carbon is oxidised thus :

$$\begin{aligned} \text{C} + \text{H}_2\text{O} &= \text{H}_2 + \text{CO}, \\ 3\text{C} + 2\text{H}_2\text{O} &= \text{CH}_4 + 2\text{CO}. \end{aligned}$$
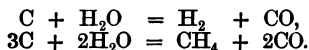
Carbon Dioxide or **Carbonic Acid** (CO_2) is a gas about $1\frac{1}{2}$ times as heavy as air, and is formed when carbon is burned in oxygen or in a free supply of air, thus : $C + 2O = CO_2$. Also when carbonic oxide is burned in air or oxygen, thus :

$$\underset{\text{Carbonic oxide.}}{\text{CO}} + \underset{\text{Oxygen.}}{\text{O}} = \underset{\text{Carbon dioxide.}}{\text{CO}_2.}$$
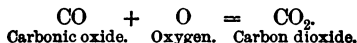
If carbon dioxide is brought in contact with red hot carbon, it takes up some of the latter, forming twice its volume of carbonic oxide (CO), thus :

$$\text{CO}_2 + \text{C} = 2\text{CO}.$$

In this case carbon dioxide is oxidising. CO_2 is not poisonous, but it will not support life or combustion.

Carbon Monoxide or **Carbonic Oxide** (CO) is a colourless gas about the same weight as air, extremely poisonous, and burns in air or oxygen with a blue flame, producing carbon dioxide and evolving considerable heat. The combustible gas formed in gas producers is chiefly CO. It is a powerful reducing agent, being the chief agent in reducing oxides, such as oxide of iron in the blast furnace, and zinc oxide in a zinc muffle. At high temperatures CO is decomposed (dissociated), especially in the presence of other bodies, such as iron, which combine with carbon. This is probably the case in the blast furnace, and in the cementation process for steel.

Phosphorus (P).—This non-metal is generally a waxy-looking crystalline solid, which readily melts and vaporises. It is highly inflammable in air, forming white vapours of phosphorus pentoxide (P_2O_5), also called phosphoric acid. It combines with oxygen in several proportions, forming the various oxides of phosphorus. These oxides unite with bases to form compounds termed phosphates. It probably exists in iron and steel as an element, but in slags as a phosphate. Thus : phosphate of iron ($3FeO.P_2O_5$) is found in tap cinder, and phosphate of lime ($4CaO.P_2O_5$) in basic slag.

Phosphates are decomposed by silica at high temperatures because under these conditions SiO_2 is more strongly acid than P_2O_5, thus :

$$3FeO.P_2O_5 \quad + \quad SiO_2 \quad = \quad 3FeO.SiO_2 \quad + \quad P_2O_5.$$
Iron phosphate.   Silica.   Iron silicate.   Phosphoric acid.
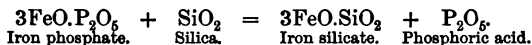
Phosphoric acid is reduced by carbon or even by iron, the phosphorus uniting with the iron, thus :

$$P_2O_5 \quad + \quad 5C \quad = \quad 5CO \quad + \quad 2P.$$
Phosphoric acid.   Carbon.   Carbonic oxide.   Phosphorus.
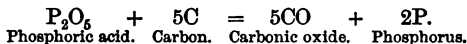
Sulphur (S) is a non-metal and a solid. It readily melts and vaporises, and unites with metals forming sulphides, such as ferrous sulphide (FeS). With oxygen it forms oxides, viz., sulphur dioxide (SO_2) and sulphur trioxide (SO_3).

Chlorine (Cl).—This element is found in nature chiefly in combination with sodium, calcium, potassium, magnesium, etc. At ordinary temperatures and pressures chlorine is a greenish-yellow gas, having a pungent and irritating smell ; but by great pressure it may be liquefied to a dark greenish-yellow liquid, and at low temperatures it may be solidified. It is readily soluble in water. It is an active chemical agent, and combines with all metals to form chlorides. It

acts indirectly as an oxidising agent by liberating oxygen from water, and is used as a disinfectant and bleaching agent. With hydrogen it forms hydrochloric acid (HCl). It plays an important part in certain processes in the metallurgy of gold, silver, mercury, and copper.

Chromium is a comparatively rare metal, which only occurs in nature in combination with other elements, the chief ore being chrome ironstone (FeO, Cr_2O_3). Chromium or its oxides form the colouring matter of several minerals; the green colour of the emerald, for example, is due to chromium oxide. The metal is obtained by the reduction of its oxide in the form of powder, by means of carbon in a lime crucible; or by the electrolysis of its chlorides, when chromium separates out in brittle glistening scales. Wöhler prepared it by fusing the sesquichloride with zinc under a layer of sodium and potassium chlorides. The zinc was afterwards dissolved out in dilute nitric acid. It may be obtained by the action of sodium amalgam on chromic chloride. By heating the amalgam of mercury and chromium formed, in hydrogen gas, the chromium is left as a spongy powder. It is tin-white in colour, having a specific gravity of 6·8. The fused metal is said to be as hard as corundum; it melts with more difficulty than platinum, and is only showly oxidised when heated in air. It is used in the form of an alloy with iron and carbon, forming a hard, white, and brilliant steel, much esteemed for special purposes.

Manganese.—The pure metal, obtained by the reduction of its oxide, is a grey or reddish-white body, hard, and brittle; its specific gravity is about 8; it is said to melt at 1900° C.; it oxidises more readily than iron, and must therefore be excluded from air by keeping it under rock-oil, or in sealed vessels. Carbonate of manganese is ignited and the oxide formed is mixed with a carbonaceous paste, well dried, and then reduced in a brasqued crucible at a very high temperature. It contains carbon and silicon, but by a second ignition under a layer of salt and nitre these are largely removed. Its chief use is in the formation of alloys with iron, steel, and copper. It is not used in the unalloyed state. Compounds of this metal are very widely distributed in nature; one of the most common is pyrolusite, or black oxide of manganese (MnO_2).

Cadmium.—In the process of zinc extraction it was observed that a volatile vapour, in some cases, was distilled off with the first portions of zinc; this was found to be the

metal cadmium. It possesses a tin-white colour, has a fibrous structure, and takes a high polish. It is harder than tin, malleable, ductile, and readily volatile. It has a density of 8·6 ; it melts at about 320° C., and boils at 860° C. Its vapour is of a dark yellow colour, with a disagreeable odour. Like tin it emits a crackling sound when bent. It is used in alloys to produce a fusible metal, which melts below 100° C., and an amalgam of cadmium is employed as a stopping for teeth, such amalgam being soft when first prepared, but soon becomes hard.

Magnesium.—This metal possesses a brilliant white colour, but soon tarnishes when exposed to moist air, due to the formation of magnesium oxide. It is stated to possess great tensile strength, being nearly equal to that of aluminium bronze. Its specific gravity is 1·74 ; it melts at 750° C. At a temperature of 450° C. it can be rolled and worked into a variety of forms. Screws and threads made of this metal are sharper and more exact than those made of aluminium. When ignited in a flame it burns with a dazzling white light, which is said to have been seen at sea from a distance of 28 miles. This light is used for purposes of photography. Magnesium occurs abundantly in nature in combination with other elements forming compounds, such as magnesite $MgCO_3$, dolomite $MgCa(CO_3)_2$, etc.

Magnesium was obtained by Davy in 1808 by electrolysis, and in 1830 Bussy obtained it by heating the anhydrous chloride with potassium. The residual chlorides were dissolved by water and the magnesium fused into globules. It is now prepared by a distillation process similar to that of zinc. The ore is roasted to oxide and reduced in retorts, which are exposed to a white heat, and the metal condensed in receivers. The retorts are made of basic material, such as bauxite or dolomite and clay. It is also prepared by electrolytic methods, using a solution of magnesium and ammonium sulphates.

The term "earth" was formerly used to denote those bodies which are insoluble or but slightly soluble in water, and unaltered by exposure to a high temperature. Some of these were found to have an alkaline reaction, and to easily neutralise acids ; hence the term "alkaline earth." These oxides—viz., baryta, strontia, lime, and magnesia—were found to be composed of metals in combination with oxygen. The alkaline-earthy metals, although their compounds are widely distributed, do not occur in nature in the metallic state, and the isolated metals have little application in the

arts, on account of the ease with which they oxidise. They may be useful in removing oxygen from other metals and their alloys.

Barium is a pale yellow metal, malleable, and fusible at a red heat. It rapidly tarnishes in air, and burns brilliantly at a red heat, forming barium oxide. Its melting point, according to Frey, is above that of cast-iron. It decomposes water rapidly at the ordinary temperature. Its specific gravity is 3·75.

Strontium is similar to barium in colour ; it is malleable, fusible at a red heat, quickly oxidises on exposure to air, burns brilliantly in air when heated, and violently decomposes water. Its specific gravity is 2·54.

Calcium is a yellow metal, tenacious and malleable ; it melts at a red heat, oxidises in air, and burns when heated ; it decomposes water rapidly. Its specific gravity is 1·58.

The word "alkali" was originally used as the name of a soluble salt obtained from the ashes of sea-plants, and is now applied to a well-defined class of bodies having the following properties :—They turn red litmus blue, completely neutralise acids, are soluble in water, and their solutions exert a caustic action upon animal matter. The alkalies proper are the oxides of sodium, potassium, lithium, rubidium, and cæsium. To these is added the hypothetical metal ammonium NH_4, which is called the volatile alkali in contradistinction to potash and soda. The metals of the alkalies are soft, readily fusible, volatile bodies, easily oxidised on exposure to air ; and they rapidly decompose water at ordinary temperatures.

Sodium.*—This metal melts at 95° C. and volatilises, forming a dark blue vapour. It rapidly oxidises in air, and when strongly heated burns with a yellow light. It decomposes water rapidly at ordinary temperatures. It is a silver-white metal, with a specific gravity of ·97. Sodium is used for the preparation of aluminium, magnesium, boron, and silicon. As an amalgam it is used in the extraction of gold, and in the laboratory as a reducing agent. It occurs very abundantly in nature in a state of combination in the forms of chloride, nitrate, borate, carbonate, and silicate.

Potassium.—This element is very similar to sodium in appearance and properties. It is a silver-white, lustrous metal, having a specific gravity of ·87 ; it is brittle at 0° C.,

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* For preparation of sodium see article on "Aluminium."

but at 15° C. it becomes soft, malleable, and weldable ; it melts at 62° C., forming a liquid like mercury in appearance ; at a red heat it boils, emitting a green-coloured vapour. It has a strong affinity for oxygen, and decomposes water at the ordinary temperature, with the production of great heat.

Lithium.—This is a widely diffused element, being found in many micas and felspars, in the ashes of some plants, and in sea-water. It has the colour and lustre of silver, is soft and weldable, melts at 100° C., is volatile when strongly heated, and burns with a white flame. It rapidly oxidises, like potassium, when exposed to air. Its specific gravity is ·58, and it is therefore the lightest of all liquid and solid bodies. Its atomic weight is 7 and its symbol Li.

Rubidium and Cæsium.—These rare metals so closely resemble potassium that they cannot be distinguished from that metal by many of the ordinary tests. Their presence is detected by means of spectrum analysis. The atomic weight of rubidium is 85·2, its specific gravity 1·52, and its melting point is 38° C. The atomic weight of cæsium is 133, its specific gravity is 1·88, its melting point 26° C., and its symbol Cs.

Chemical Affinity.—The distinctive character of each element is found in its capacity to combine with other elements and form chemical compounds. Thus chlorine combines readily with all the metals, while oxygen does not directly combine with certain of them, such as gold and platinum, and when it is caused by indirect means to enter into combination, the compounds are not very stable. The cause which influences elements and compounds to unite with each other and remain in combination is termed *Chemical affinity.* It differs from gravity in that it acts at infinitesimal distances, and from cohesion in that it acts between the fundamental components of a compound and not upon a substance as a whole. Formerly, the idea of chemical affinity was associated with electrical polarity, and the elements were classified into + and − bodies, and the more electro-positive an element was, the more readily it was assumed to combine with an electro-negative body. If water is decomposed by electricity, the hydrogen appears at the negative pole, hence it was termed an electro-positive body ; and conversely, oxygen was considered an electro-negative body because it appears at the positive pole. The electrical theory still survives in the explanation generally given of the transmission of an electric current through a

solution by alternate decomposition and recomposition of the individual molecules. That the electric polar theory of chemical affinity is open to objection is shown by the discovery of Dumas and Laurent that chlorine is able to replace and displace hydrogen in many organic compounds, *i.e.* an electro-positive by an electro-negative element, which is not in accordance with this theory.* The substitution of chlorine for hydrogen has been termed Metalepsis.

Chemical changes are effected by the internal movements of the component particles of a body, and the total result is the sum of the results of the motions of the individual particles. Heat, light, and electricity are also forces due to molecular motion, hence the possibility of transforming one kind of movement into that of another kind. This interchange has resulted in the general belief that force, like matter, is indestructible, hence the *Conservation of energy.* The mutual convertibility of one kind of energy into another kind does not prove that all kinds of energy are the same, but that when a certain amount of one kind of energy, say chemical, disappears, an equivalent amount of another kind, say heat, is generated. It will afterwards be pointed out that heat energy is probably concerned with molecules and chemical energy or affinity takes place between atoms, and that one kind of movement profoundly influences the other. The conversion of chemical into heat energy is seldom, if ever, complete, especially, as in some cases, bodies like charcoal and sulphur unite with absorption of heat. Chemical reactions are therefore, in some cases, *endothermal,* heat being absorbed; but in most cases they are *exothermal,* heat being evolved. In the combustion of the different forms of carbon the calorific effect is greater with charcoal than with the diamond, because the bonds which hold the atoms of the latter together are stronger than those in the former, and more heat is therefore absorbed in the mechanical work of unlocking these bonds. Every element appears to have a different store of available energy, thus gold, platinum, nitrogen, etc., seem to have very little, while oxygen, chlorine, potassium, etc., seem to be endowed with a great supply. Chemical reactions are influenced by external heat, and the amount of this heat which is absorbed before the change occurs, termed *Specific heat,* prepares, as it were, the molecules for the reaction.

Some reactions between bodies are reversible, while others are non-reversible. The action of oxide of iron in the blast

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* See Mendeleef's *Chemistry,* Vol. I., p. 465.

furnace is a good illustration of the former. Take the following equations :

$$Fe_2O_3 \quad + \quad 3CO \quad = \quad 2Fe \quad + \quad 3CO_2$$
$$2Fe \quad + \quad 3CO \quad = \quad Fe_2O_3 + \quad 3C.$$
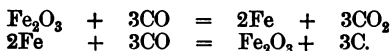
In the first equation, carbonic oxide reduces oxide of iron and is itself oxidised to carbon dioxide, while in the second equation the carbonic oxide acts in the opposite manner and oxidises metallic iron. Evidently at a certain point equilibrium is established, and beyond that point the former reaction is reversed. The reduction of oxide of iron by carbonic oxide begins at 150° C. and proceeds up to the limit, when reduction ceases and oxidation begins. At a white heat another reversal takes place, and the oxide of iron is completely decomposed. Chemical combination only takes place when a certain temperature is reached, so that the affinities are weakened and the formation of new compounds rendered possible. Chemical decomposition absorbs heat because the chemical energy is transformed into mechanical energy at the expense of heat, hence all chemical compounds are decomposed at a sufficiently high temperature. At very low temperatures chemical reactions are probably impossible.

Although in all cases a certain maximum temperature is necessary for complete decomposition, a certain portion of a compound may be decomposed at a much lower temperature and the amount may gradually increase up to a maximum, when complete decomposition ensues. This partial decomposition is termed *dissociation*. If the products of dissociation are removed as they are formed, then the body may be completely decomposed ; but if the products remain in contact with the undecomposed part, a limit will be reached when no further decomposition will occur, and then, if the pressure of the products increases, recombination will begin. This is the case in the Deville furnace for melting platinum by the oxy-hydrogen blow-pipe, where the oxygen and hydrogen, which have produced a high temperature by their union, are, at a certain pressure, decomposed again, thus limiting the possible temperature attainable. Our knowledge of the phenomena of dissociation is due to H. St. Claire Deville, who also showed that the initial temperature of dissociation is near to the initial temperature of combination.

Chemical action has been indicated above as a motion between the fundamental particles of a body, hence the degree of affinity between two reacting bodies is generally influenced by the condition of contact. Thus two solids act

more perfectly on each other when in the state of a fine powder, because the points of contact are multiplied, and Spring has shown that powders which do not act on each other at the ordinary temperature may undergo reaction under an increased pressure. He caused sulphur and metals to unite with each other by subjecting their powders to very great pressures. It will easily be seen that bodies when in a liquid or gaseous state act more vigorously on each other than the same in a solid state, because of the more intimate contact between the particles.

Atoms and Molecules.—Atoms are the smallest possible particles of elements, and therefore indivisible, which can unite to form complexes, termed molecules. As already stated, they have weights and the sum of their weights forms the weight of the molecule and the sum of the weights of the molecules forms the weight of the mass, and is the cause of gravity and of all the phenomena which depend on the mass of a substance. Now, as the weight of an atom is the minimum quantity of an element entering into the composition of the molecules formed by it, we may find the weight of the atom by determining the amount in any of the known molecules thus :

	Formula.	Molec. Weight.	Amount of Oxygen.	Amount of Hydrogen.
Water, . . .	H_2O	18	16	2
				Amount of Carbon.
Carbonic oxide, . .	CO	28	16	12
Carbon dioxide, . .	CO_2	44	32	12
				Amount of Sulphur.
Sulphur trioxide, .	SO_3	80	48	32

In the above cases we see that 16 is the smallest quantity of oxygen capable of entering into the composition of a chemical compound, and that any other portion entering into combination is an exact multiple of 16—therefore 16 is the atomic weight of oxygen. When a molecule is divided by any means the atoms do not generally fall apart like grains of sand, but arrange themselves in fresh groups. In fact, as a general rule, atoms do not exist in the free state, but form molecules containing at least two atoms. An element contains molecules composed of atoms of the same kind, while a compound consists of molecules containing atoms of two or more kinds. Some metals, such as zinc, cadmium, and mercury, consist of free atoms and therefore contain only

one atom in the molecule.   Molecules are capable of uniting
into groups, and any influence that causes an alteration in
the molecular grouping modifies the physical properties of the
metal.   A very small quantity of impurity will influence the
molecular grouping, hence an impure metal always has some-
what different properties to that of a pure metal.   The
molecules of some metals split up into single atoms when
they are volatilised, and it is probable that many pure metals,
such as gold, silver, copper, and iron, have a simple atomic
constitution, and therefore their masses may be regarded as
single molecules.   If an impurity, or an external force,
causes the atoms to unite and form complex molecules, the
mass of the metal will probably be less tough.

The various elements do not all unite with each other
with the same number of atoms, and while one atom of
silver may replace one atom of hydrogen, one atom of copper
is capable of replacing two atoms of hydrogen, and so on up
to a certain limit, which is usually not greater than six.   This
has led to a classification of elements into six or more types,
and each element is said to have a valency of one or more
according to the type to which it is assigned.   It must not be
assumed that any given element has only one valency, but
that as a general rule, and under what may be termed ordinary
conditions, it acts as though the valency were thus limited.
Hydrogen, chlorine, silver, potassium, etc., are said to have
a valency of one, because, if they unite with each other at
all, they usually unite with an equal number of atoms, hence
the formula for hydrochloric acid is HCl, and potassium
chloride KCl.   Oxygen has a valency of two, therefore it
may unite with two atoms of hydrogen or chlorine.   Carbon
has a valency of four, therefore it may unite with four atoms
of hydrogen or chlorine, and with two atoms of oxygen.
The elements, silver, oxygen, and carbon, are therefore said
to be univalent, bivalent, and tetravalent respectively.   The
following formulæ will illustrate the above remarks :

$$HCl \quad H_2O \quad H_3As \quad H_4C \quad H_4ClN \quad SO_3.$$
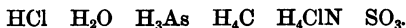
The term atomicity is generally used to signify the
greatest number of atoms of one kind or another with which
a given atom is ever observed to be united, but it does not
indicate that a tetravalent element, for example, is capable
of uniting with four atoms of every univalent element, since
the capacity of any element for combination depends on the
nature of the element with which it may be in contact.

By observing the composition of corresponding compounds

the *equivalent weights* of the metals may be determined. It will be found that different metals may displace different amounts of hydrogen from an acid, according to their valencies. If the valency of a metal, such as sodium, is one, then one atom will replace one atom of hydrogen. If the valency is two, it will set free two atoms of hydrogen, and so on. Hence the equivalence of any element may be numerically stated by dividing its atomic weight by its valency. Thus silver is 108, copper is $\frac{63}{2}$, gold is $\frac{196 \cdot 2}{3}$, tin is $\frac{118}{4}$, and so on. If, therefore, the same electric current is passed through water, silver solution, copper solution, gold solution, and a tin solution, then for every part by weight of hydrogen liberated from the water there will be deposited 108 parts of silver, 31·5 parts of copper, 65·4 parts of gold, and 29·5 parts of tin by weight respectively.

The term specific heat has already been defined. It has been observed that the specific heats of elements in the solid state decrease as the atomic weights increase, and that the product of the specific heat of an element into its atomic weight is an almost constant quantity. The atomic heats of all elements are therefore practically the same, *i.e.* the amount of heat required to produce the same change of temperature in the different elements is the same when the quantities operated upon are in the proportion of their atomic weights. For thermal changes the atom is the unit, and all atoms, notwithstanding the difference of weight, are equal in this respect. This is Dulong and Petit's law.

Thermo-Chemistry.—It has been shown that combustion is the result of chemical action, and that the general effect of chemical action is an evolution of heat, but in some cases heat is absorbed. In the combination of oxygen with different elements, for example, different quantities of heat are generated : $Na_2 + O$ yields 100000 units of heat ; $H_2 + O$
46 16
yields 69000 units ; $Fe_2 + 3O$ yields 64000 units ; $Zn + O$ yields 86000 units ; $Pb + O$ yields 51000 units ; $Cu + O$ yields 38000 units ; $Hg + O$ yields 31000 units. Now, although this shows a difference in the affinities of the above metals for oxygen, it does not express the magnitude of the affinities. The above figures, however, may be taken to indicate in a general manner the relative affinities of those elements, for the formation of mercury oxide which yields the least heat is the least stable and the most easily decomposed, while sodium oxide is the most stable, and sodium is able to decompose

all the other oxides and unite with the oxygen. Thomsen considers that only those chemical reactions take place of their own accord in which the greatest amount of chemical energy is transformed into heat. But we have insufficient evidence at present of the exact proportion of the total heat
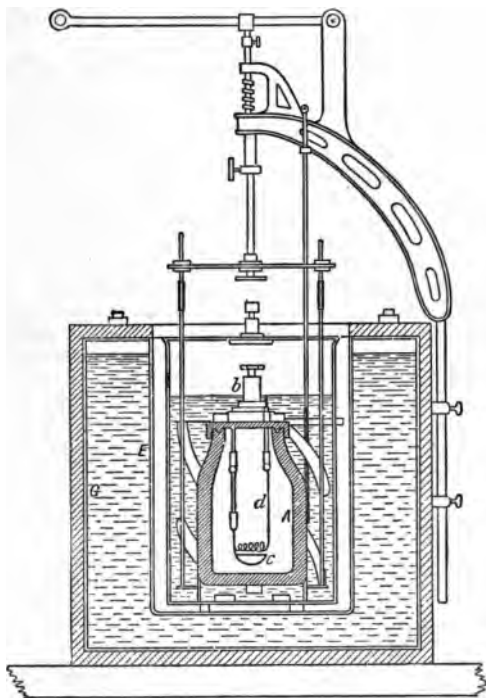
Fig. 11.

produced which is due to the chemical action. Moreover, in many cases there are endothermal reactions which proceed under the same circumstances as exothermal, such as carbon which burns in sulphur vapour and absorbs heat, while the same burns in oxygen and evolves heat. Mendeleef states that the objections to the acceptance of

thermo-chemical data as facts are : (1) Many determinations
are made in weak solutions, and water is not a simple
diluting substance, but acts in many cases chemically on
the substance dissolved.   (2) Determinations made at high
temperatures are unreliable unless we know the specific
heat of the bodies at those temperatures.   (3) Physical and
mechanical changes (change of volume, diffusion, etc.) pro-
ceed side by side with chemical changes.

The Berthelot-Mahler bomb calorimeter (Fig. 11) has been
specially devised for calorimetric measurements.   It consists
of a steel shell A of about 40 cubic inches capacity, nickel
plated on the outside and enamelled on the inside.   The
top is closed by a screw cap provided with a cock B for
admission of compressed oxygen.   A platinum rod attached
to the cap supports a platinum cap C, in which the fuel to
be tested is placed, and the ignition is effected by the heat
of the wire D, which conveys an electric current.   The com-
bustion and products of combustion being confined to the
inside of the bomb, the heat is transmitted through its walls
to the water in the vessel E surrounding the bomb.   In
order to get a uniform temperature a helical agitator is
employed as a stirrer.   An outer vessel G, covered exter-
nally with felt, also contains water and is provided with
a thermometer for registering the initial and final tempera-
tures.   For solid or liquid fuel a gramme is generally
taken.   For determining the calorific power of a gas of
constant volume, the bomb is exhausted of air, filled with
the gas, again exhausted, and finally refilled at the atmo-
spheric pressure.   Ignition is effected as before, and the
heat absorbed by the water.

Thermal equations may be conveniently employed to repre-
sent the final heat produced in chemical combinations.   The
− sign placed before the heat units signifies that heat in
that case has been absorbed, thus :

$$ZnO + C = Zn + CO.$$
$$86400 \qquad\qquad 29000 - {} - 57400 \text{ units.}$$
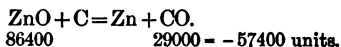
The number 86400 is the amount of heat absorbed in the
decomposition of 81 grammes of zinc oxide, and 29000 the
amount of heat produced in the formation of 28 grammes
of carbonic oxide.   The heat absorbed in the decomposition
of a compound is equal to the heat produced in its forma-
tion, provided the initial and final states are the same.
This is a special case under a general principle which
may be stated thus : Whenever a system of bodies under-

goes chemical or physical changes, and passes into another condition, whatever may have been the nature or succession of the changes, the quantity of heat evolved or absorbed depends on the final conditions of the system, provided no mechanical effect has been produced on bodies outside. The equation mentioned above, in order to be rigidly accurate, should be corrected to the temperature at which the reaction occurs. It will be observed that the reaction is endothermic, and these are more frequent at high than at low temperatures. The following equations may be taken as types to illustrate the foregoing remarks : *

$$HgS + O_2 = Hg + SO_2.$$
$$8200 \qquad\qquad\qquad 71000 \quad - \quad 62800 \text{ units.}$$

$$CuS + 2CuO = 3Cu + SO_2.$$
$$10200 \quad 2 \times 37200 \qquad\qquad 71000 \quad - -13600 \text{ units.}$$

$$PbS + Fe = Pb + FeS.$$
$$17800 \qquad\qquad\qquad 23800 \quad - \quad 6000 \text{ units.}$$

$$Fe_2O_3 + 3CO = 2Fe + 3CO_2.$$
$$199400 \quad 3 \times 29000 \qquad\quad 3 \times 97000 - \quad 4600 \text{ units.}$$

$$CuSO_4 + Fe = FeSO_4 + Cu.$$
$$182600 \qquad\qquad 235600 \qquad - \quad 53000 \text{ units.}$$
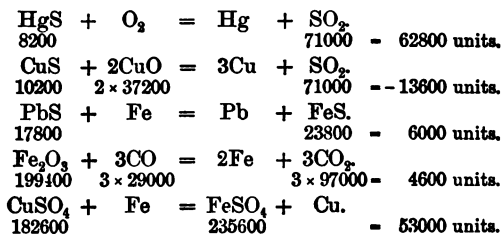
Solution.—The solvent power of water is familiar to everybody, and all liquids possess the same power in a greater or less degree. Any given solid is not soluble in all liquids, neither can any one liquid dissolve every solid. As a general rule, the dissolving power of each liquid is confined to a certain class of solids. Thus water readily dissolves saline substances, mercury dissolves most metals, alcohol dissolves resins, and ether dissolves fats. Water is the chief solvent in nature, and becomes the medium of many chemical changes. It appears to be a general rule that the solubility of a body in any medium often depends on a similarity in constitution of the body and the solvent. Again, as a general rule, the solvent power of a liquid increases as the temperature rises ; thus acids dissolve metals more readily when heated than when cold. When a liquid has dissolved all of a solid that it is capable of retaining at a given temperature, it is said to be saturated ; but when it is saturated with one solid it may still be capable of taking up another, and in some cases the solvent power is thereby increased. When a solid dissolves in a liquid there is a change of temperature, and if the

* For fuller information, see *Introduction to Metallurgy*, Roberts-Austen, p. 289.

solution thus formed is diluted by an addition of more
of the liquid a further change of temperature occurs,
but the thermal change gradually becomes less by each
addition.

Two classes of theories have been advanced to account for
the act of solution—(1) Chemical combination between solvent
and body dissolved ; (2) adhesion of the solid to the liquid,
and mechanical intermixture of the two kinds of molecules.
Probably the truth lies in both views.   Some bodies retain
their chemical identity, while other bodies become totally
changed, as, for instance, when copper dissolves in nitric acid.
In many cases a mixed effect occurs, and we may conceive of
every degree of gradation between that of a definite chemical
union and that of a simple solution, such as sugar in water.
The metallic alloys are good illustrations of the above re-
marks.   They may be considered as solutions of one metal in
another, often modified by chemical affinities which tend to
form definite chemical compounds.

The subject of crystallisation is closely allied with that of
solution, as it is in the passage from the liquid to the solid
state that crystals are most generally formed ; for when the
percentage of a solid present in a solution exceeds its limit
of solubility then, by lowering the temperature or by evapor-
ating the solution, crystals are usually formed, and these
frequently retain a portion of the solvent.   In the case of
aqueous solutions, the water thus retained is termed water
of crystallisation.   Certain solutions may be cooled down
below the point at which crystallisation naturally begins,
without alteration ; they are then said to be supersaturated.
If a crystal of the same kind be dropped in, the whole
solution will rapidly crystallise.   Shaking the solution often
effects the same result.   Molten metals, such as tin, gold,
etc., may be cooled below their freezing points, but the
slightest touch will cause them to solidify.

Most liquids dissolve gases, and under the same conditions
the volume of gas dissolved in a given liquid is always the
same, but it varies with the pressure of the gas on the surface
of the liquid, with the temperature, and with the nature of
the gas and of the absorbing liquid.   Henry and Dalton's law
states that the weight of a gas dissolved by a liquid is directly
proportional to the pressure.   But this rule ceases to hold
good when the gas and liquid exert a chemical action on each
other, and also in the case of an easily liquefiable gas.   Most
liquids when rapidly solidified retain more or less of the dis-
solved gas, which renders the proper casting of many metals

a difficult operation, requiring the highest skill and great experience to produce soundness.

Closely connected with the phenomena of solution is that of diffusion. If two liquids of different densities be carefully put into the same vessel they will gradually interpenetrate each other in opposition to gravity. This diffusive power depends on the motion of the molecules peculiar to each liquid. Some liquids are incapable of mixing together, such as oil, mercury, and water. Graham divided all bodies, as regards diffusive power, into two classes—(1) Those which diffuse readily through a given liquid menstruum are termed crystalloids ; (2) those which are little diffusible, like glue, are termed colloids. The rate of diffusion increases with the temperature, and, when the solution is not too concentrated, is proportional to the strength of the solution. Colloids are believed to consist of molecules having far more complex atomic aggregates than those of crystalloids, and are therefore heavier and move more slowly.

Allotropy.—Many elements exist in more than one form, each state conferring different properties. This is ascribed to the different grouping of the atoms in the molecule. Diamond, graphite, and charcoal have each distinct properties due to the peculiar aggregation of the atoms in each case, yet they are chemically the same substance. One of the characteristic features of allotropic states is the difference in volume, and often in crystalline form. When the crystals belong to two different systems the body is said to be dimorphous, and if to three different systems, trimorphous, etc. Such phenomena are termed polymorphism, and are merely one of the characteristics of allotropy. Lead when cast has different properties to electro deposited lead, the latter being rapidly oxidisable, and may be readily crumbled to powder. Tin, when exposed to extreme cold, falls to a grey powder. Roberts-Austen has shown that gold, when released from an alloy of potassium and gold by means of water, is in the form of a black powder which is slightly soluble in water. Some metals, such as iron, when released from their amalgams, take fire spontaneously in air, and thus act quite differently to what they do in the ordinary condition. Aluminium, which does not oxidise in air, soon takes up oxygen when coated with a layer of mercury, which probably modifies its molecular condition. It has already been shown that a very small quantity of an impurity added to a metal may also modify its atomic aggregation, and thus greatly alter its properties. For example, ·1 per cent. of bismuth in

D

copper will enormously reduce its conductivity, ductility, etc., and make it worthless for many purposes where these properties are important.

Periodic Law.—Mendeleef has shown that the properties of the chemical elements are definitely related to their atomic weights. If we write down the names of the elements in the order of their atomic weights, beginning with the lowest, which is hydrogen, we find at certain points in the chain a recurrence of properties, with a gradual waning to a minimum and then a gradual waxing to a maximum in certain properties of the elements which occupy the intermediate positions. The law states that the properties of the elements are a periodic function of their atomic weights. Lothar Meyer extends the law to atomic volumes, and considers that there is an intimate relation between the atomic volumes of the elements. The volume occupied by an atom cannot be measured, but if quantities of different elements proportional to their atomic weights be taken, and the space occupied by these quantities compared, the relative volumes may be obtained. The atomic volume of an uncombined element in a liquid or solid state is assumed to be in direct proportion to the atomic weight, and inversely proportional to the density ; hence

$$\frac{\text{atomic weight}}{\text{density}} = \text{the atomic volume.}$$

Take gold, for example : $\frac{196\cdot2}{19\cdot3} = 10\cdot2$, the atomic volume, *i.e.* 196·2 grammes of gold occupies a space of 10·2 centimetres. In the following curve (Fig. 12), the atomic weights and atomic volumes are represented as co-ordinates. It shows the gradual waxing and waning of density and of atomic volume, and these variations are accompanied with similar changes in valency, basic and acid character of the oxides, and tendency to combine with chlorine and hydrogen, etc. Roberts-Austen has shown that not a single element which occupies a position at the base of either of the above loops diminishes the tenacity of gold when present in small quantity, and that all elements which occupy high positions on the loops tend to render gold fragile. Osmond has convinced himself that the effect of a given element in retarding or promoting the passage of iron to an allotropic state is in accordance with the Periodic Law.*

* See *Principles of Chemistry*, Mendeleef, Vol. II., English translation.

PERIODIC LAW

Fig. 12.
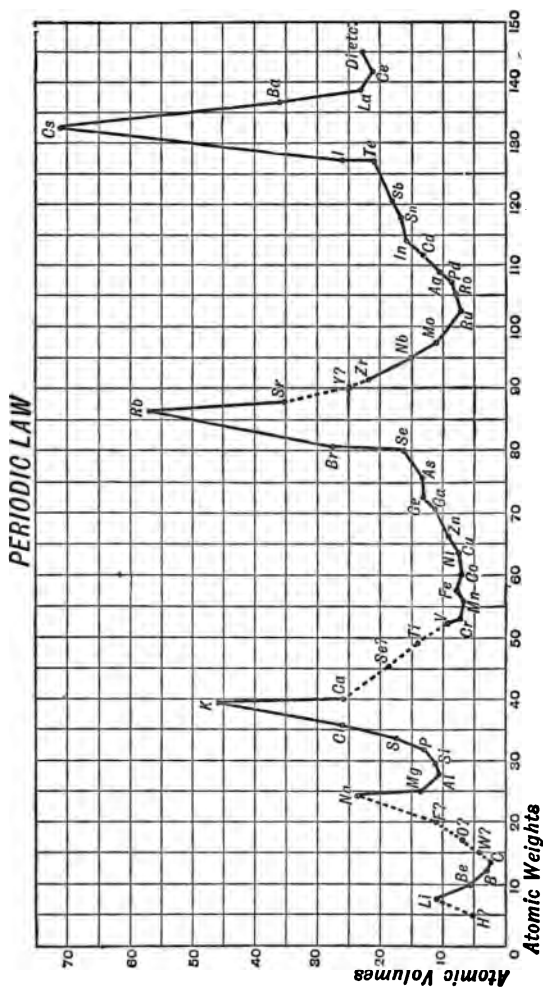
CHAPTER IV.

ALLOYS.

By uniting two or more metals in various proportions an almost endless variety of combinations may be obtained, possessing more or less the properties of their constituents. In some cases the properties of the resulting combination are totally different from either of the components. The general effect of alloying metals together is to increase the hardness, lower the melting point and conductivity, and otherwise modify the properties of the separate metals. The word "alloy" probably is derived from the Latin, *alligo*, "to bind to." An illustration of the hardening power by alloying is seen in the case of standard gold and silver ; of the lowering of melting points in the case of Wood's fusible alloy and in ordinary soft solder. The class of alloys known as brass forms a good object lesson in varying changes of colour produced by alloying. The colouring power of different metals in affecting the colour of alloys is stated by Ledebur to be in the following order : Tin, nickel, aluminium, manganese, iron, copper, zinc, lead, platinum, silver, and gold. Each metal in this list has a greater decolorising action than the one succeeding it.

The specific gravity of an alloy nearly always differs from the mean of the specific gravities of its constituents, sometimes being greater and sometimes less. When the density has increased it shows that contraction has occurred, and chemical combination has probably taken place between the whole or some portion of the constituents. This is the case with bronzes rich in copper, but with bronzes rich in tin expansion occurs, and the specific gravity is less than the mean of the components. One of the greatest difficulties connected with the subject of alloying is the tendency of the constituents, or certain portions of the constituents, to

separate on cooling from the molten state and thus to produce heterogeneity. In fact, a cooling mass of mixed metals often behaves like water containing suspended matter does in freezing, when the ice first formed rejects the impurities. Thus when a molten mixture of lead and bismuth is allowed slowly to cool, a certain alloy of the metals solidifies first, and the most fusible alloy of the series is left. Guthrie called this the "eutectic" alloy. As a rule this defect is intensified when several metals are required to be alloyed, especially when they differ widely in fusibility. The separation during cooling before solidification is to some extent prevented by mechanical agitation, such as stirring with a rod ; and by pouring the metal into the mould at as low a temperature as is consistent with the proper degree of liquidity.

Most metals are capable, to some extent, of existing in a state of chemical combination with each other, but, as a rule, they are united by feeble chemical affinities, for it is necessary, in order to produce energetic union, that the constituents should exhibit great dissimilarity in properties. It is certain that metals can unite in definite proportions, but it is difficult to obtain these compounds in a separate state, since they dissolve in almost all proportions in the melted metals and do not differ so widely in their melting points from the metals in which they are dissolved as to be separated by crystallisation in a definite condition.

Matthiessen considers it probable that the condition of an alloy of two metals in a liquid state is either (1) a solution of one metal in another ; or (2) a chemical combination ; or (3) a mechanical mixture ; or (4) a solution or mixture of two or all of the above ; and that similar differences may obtain as to its condition in the solid state. A solidified solution of one metal in another is well exhibited in the alloys of lead and tin. Examples of chemical combination are seen in the alloys of copper and tin containing 61·6 per cent. of copper, and represented by the formula $SnCu_3$, also in certain amalgams, such as $AgHg_3$, and in the alloy of gold and tin $SnAu_2$. Lead and zinc, and silver and lead, are examples of mechanical mixtures.

Alloys are generally prepared by fusion in a crucible, but they may be prepared by strongly compressing their powders. Certain alloys, such as gold and copper, or copper and zinc, may be made by electro deposition. Rich aluminium alloys are prepared on the large scale by the action of a powerful electric current. Of these three

methods the first is by far the most important and most
useful in its application.   It is customary to first melt
the metal which has the highest melting point, and then add
the other constituents.   In addition to the heat produced by
the fuel in the furnace, there is sometimes heat produced by
the chemical combination between the alloying metals.   This
is the case with aluminium and copper, arsenic and anti-
mony, bismuth and lead ; but when lead and tin unite heat
is absorbed.

With regard to the action of an electric current on molten
alloys, no electrolytic separation takes place by the passage
of an electric current similar to that in an ordinary saline
solution—the alloys simply act as conductors.   Matthiessen

Fig. 13.
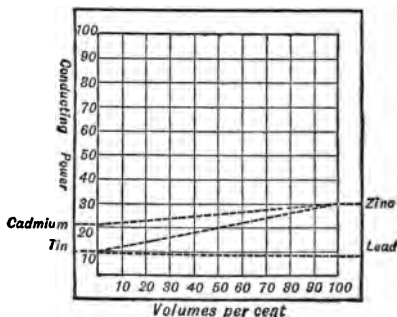
has divided metals in the solid state into two classes as
regards conductivity : *

" A. Metals which, when alloyed with each other, conduct
electricity in the ratios of their relative volumes—lead, tin,
zinc, and cadmium.

" B. Metals which, when alloyed with each other, or with
a metal of class A, do not conduct electricity in the ratios
of their relative volumes, but always in a lower degree than
that calculated from the mean of their volumes—bismuth,
antimony, platinum, palladium, iron, aluminium, gold,
copper, silver, etc.

" The curves representing the conductivity of different
series of alloys have the relation shown in the accompany-
ing diagrams.

* Watt's *Dic. of Chem.*, Vol. III., pp. 943, 944.

"Group I. Those belonging to the alloys of metals in class A are almost straight lines. That of lead-tin alloys is given as a type (Fig. 13.)
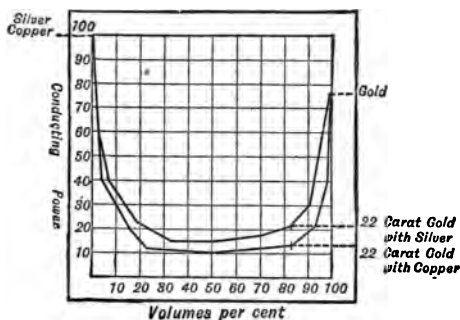
Fig. 14.

"Group II. The curves of alloys of metals in class B show a rapid decrement on both sides of the curve, the turning points being connected together by nearly straight lines. That of gold-silver alloys is given as the type. (Fig. 14).
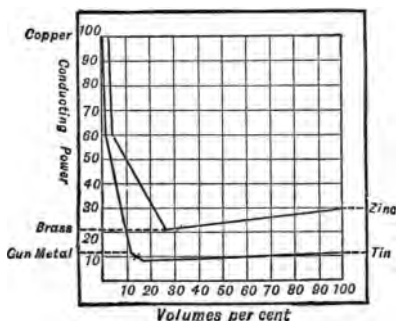
Fig. 15.

"Group III. The curves of alloys of metals in class A with those in class B show a rapid decrement on the side beginning with the metal belonging to class B, then turning

and going in a straight line to the other side, beginning with metal belonging to class A. That of tin-copper alloys is given as the type (Fig. 15).

"The influence exercised upon the conductivity of metals by the presence of small quantities of other metals, does not appear to be in any way determined by the alteration of crystalline form, or tendency to crystallise, which are known to be influenced by that circumstance.

"If it be assumed that the metals belonging to class B undergo a molecular change when alloyed with one another, or with metals belonging to class A, and that in each case an allotropic condition is induced by a small amount of other metals, varying with the different metals, then many of the phenomena characteristic of alloys may be explained."

Professor Dewar and Professor Fleming have determined the conductivity of alloys at very low temperatures, and found that many of those alloys which are poor conductors and therefore offer comparatively great resistance to the passage of an electric current at the ordinary temperature, have the same property but little diminished at $-100°$ to $-200°$ C.

When it is desirable to add a non-metallic element to a metal or alloy, for the purpose of bringing about a certain result, very much greater care is generally required in apportioning the quantity to be added than is generally the case with another metal, as non-metals combine much more actively with metals than the metals do with each other, and a very small quantity of a non-metal will suffice to alter the properties of a metal or alloy. It is very surprising to note how, in some instances, a mere trace of another element will alter the properties of a metal. For example, $\frac{1}{500}$ part of carbon added to iron will convert it into mild steel, and $\frac{1}{1000}$ part of phosphorus will make copper hot-short. $\frac{1}{2000}$ part of tellurium in bismuth makes it minutely crystalline; $\frac{1}{1000}$ part of antimony in copper renders it exceeding bad in quality for certain purposes.

Lothar Meyer has shown that a remarkable relation exists between the "atomic volumes of the elements." As before stated, the relative atomic volumes of the elements are found by dividing their atomic weights by their specific gravities. It would appear that the power of an element to produce weakness in another metal, when added in small quantity, is dependent on the atomic volume of the impurity.* Roberts-Austen tried the effect of various

* See Chapter III., p. 50.

elements on pure gold, and found that when the body added had an atomic volume equal to or less than that of gold, the strength was little affected, and in some cases, such as copper, for example, was increased; but when the element added had an atomic volume much greater than that of gold the strength was greatly diminished. His results are embodied in the following table :

	Tensile strength.	Elongation per cent on 3 inches.	Impurity per cent.	At vol. of impurity.
K, . .	{ Less than ·5	Not perceptible.	Less than } ·2 }	4·51
Bi, . .	·5	,,	·21	20·9
Te, . .	3·88	,,	·186	25·5
Pb, . .	4·17	4·9	·240	18
Thallium, .	6·21	8·6	·193	17·2
Sn, . .	6·21	12·3	·196	16·2
Sb, . .	6·0	?	·203	17·9
Cd, . .	6·88	44·0	·202	12·9
Ag, . .	7·1	33·3	·2	10·1
Pa, . .	7·1	32·6	·205	9·4
Zi, . .	7·54	28·4	·205	9·1
Rh, . .	7·76	25·0	·21	8·4
Mn, . .	7·99	29·7	·207	6·8
In, . .	7·99	26·5	·29	15·3
Cu, . .	8·22	43·5	·193	7·0
Li, . .	8·87	21·0	·201	11·8
Al, . .	8·87	25·5	·186	10·6

Copper Alloys.—*Brass* is one of the most important alloys of copper, and the term may be used to signify all combinations of which copper and zinc are the chief constituents. These metals mix together in all proportions forming alloys of various shades of colour, ranging from the red of copper at one end to the bluish-white of zinc at the other end. Thus, alloys containing 94 to 99 per cent. of copper are red ; with 87 to 93 per cent. of copper the colour is reddish-yellow (gilding metal) ; from 79 to 84 per cent. of copper a yellowish-red tint prevails ; below this, down to 50 per cent. of copper, the colour consists of various shades of yellow ; and with less copper than this the colour of the zinc gradually overpowers the red of the copper, the alloy becoming lead-like in appearance. The best varieties of brass are exceedingly malleable and ductile, and possess brilliant

lustre ; they are harder than copper, the hardness increasing
with the proportion of zinc.   Brass with 58 to 62 per cent.
copper is termed Muntz' or yellow metal, and can be rolled
hot, while the better qualities are not malleable at a red heat.
By continued vibrations or stress a crystalline structure is
induced in hard brass which makes it brittle.   Brass is pre-
pared by first melting the copper in a plumbago crucible
and cautiously adding the zinc, which should be previously
heated.   A little lead is added to brass required for turning.
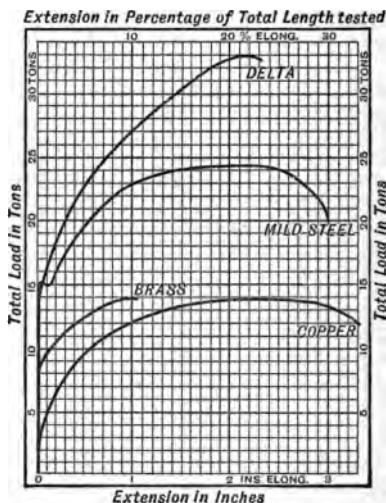
Fig. 16.

When the above yellow metal contains 1 to 3 per cent. of
iron and manganese, which makes it much harder, it is
known as Aich's metal, sterro metal, and delta metal.   Some-
times a little phosphorus is added.   Fig. 16 shows the relative
tensile strengths and elongations of delta metal compared
with some other metals.

Brass Solders are copper-zinc alloys employed for joining
the various parts of articles together by fusion.   The solder
must, therefore, have a lower melting point than the body
to be soldered, but the fusing point of the solder should

Some Varieties of Modern Brass.

Name.	Colour.	Copper.	Zinc.	Tin.	Lead.	Iron.	Gold.
Jewellers' gilding alloy,	Red,	94	6	...	...	...	...
,, ,,	,,	90·5	7·9	...	1·6	...	...
Pinchbeck,	Reddish-yellow	88·8	11·2	...	...	...	...
,,	Red,	93·6	6·4	...	...	...	...
Orëide (French gold)	Reddish-yellow	90	10	...	...	...	...
Talmi gold,	Gold,	90·70	8·33	...	...	...	·97
Tissier's metal, with one per cent. of arsenic,	Red,	97	2	...	...	...	...
Tournay's alloy,	Yellow,	82·54	17·46	...	...	...	...
Rich sheet brass,	,,	84	16	...	...	...	...
Bath metal, similor, etc.,	,,	80	20	...	...	...	...
Dutch alloy,	,,	76	24	...	...	...	...
Bristol sheet-brass,	Bright yellow,	72·8	27	...	·2	...	...
Brass wire,	,,	70	30	...	...	...	...
Orëide,	,,	68·21	31·07	·48	...	·24	...
Prince's metal,	Yellow,	75	25	...	...	...	...
Sheet and wire brass	Full-yellow,	67	33	...	...	...	...
Mosaic gold, ordinary brass,	,,	66·6	33·3	...	...	...	...
Bobierre's metal,	,,	66	34	...	...	...	...
Muntz' metal,	,,	62	38	...	...	...	...
,, ,,	,,	60	40	...	...	...	...
Gedge's metal,	,,	60	38·5	...	...	1·5	...
Common brass,	,,	64	36	...	...	...	...
Aich's metal,	,,	60	38·2	...	...	1·8	...
French brass (potin jaune),	Gray-yellow,	71·9	24·9	1·2	2·0	...	...
Hamilton's metal, chrysorin,	Full-yellow,	64·5	32·5	·3	2·7	...	...
French brass for fine castings,	,,	71	24	2	3	...	...
Sterro metal,	...	55·5	42	...	...	2·5	...
Hard solder for copper or iron,	...	57	43	...	...	...	...
Hard solder for brass	...	50	50	...	...	...	...
Dipping brass,	...	53	47	...	...	...	...
White brass,	...	33	66	...	...	...	...
Lap alloy,	...	12·5	87·5	...	...	...	...

approach, as nearly as it conveniently can, to that of the article, as a more perfect and more tenacious junction may thus be effected. Brass solder belongs to the class known as hard solders, or brazing solders. It may be stated as a

general rule that the melting point of copper-zinc alloys is higher in proportion to the amount of copper present, and therefore any quality of brass may be made into a suitable solder by adding zinc or copper as the case may be.

	Composition.		Percentage of tin.		Percentage of tin in the portion last solidified.	Physical properties.
	Cu.	Sn.	top.	bottom		
1. CuSn₅,	9·73	90·27	87·87	92·9	98·50	Tin-gray, soft as tin, non-crystalline.
2. CuSn₃,	15·21	84·79	83·15	78·90	96·99	Tin-gray, crystallising by slow cooling.
3. CuSn₂,	21·21	78·79	74·97	77·4	94·40	Tin-gray, crystallised moderately hard.
4. CuSn,	34·99	65·01	55	80	82·83	Whitish - gray, crystalline and brittle.
5. Cu₂Sn,	51·84	48·16	—	—	50·42	Bluish-gray like zinc, crystalline, very brittle.
6. Cu₃Sn,	61·79	38·21	37·29	37·66	37·37	Bluish, fine-grained, pulverisable in a mortar.
7. Cu₄Sn,	68·28	31·72	30·44	30·83	30·91	White, laminar, brittle as glass.
8. Cu₅Sn,	72·91	27·09	27·15	26·78	27·76	White, with yellow reflex, crystalline, very hard.
9. Cu₆Sn,	76·31	23·69	23·37	23·69	25·17	Yellowish, very hard, fine-grained, malleable at dull red heat.
10. Cu₇Sn,	79·02	20·98	21	21·32	24·85	Like No. 9.
11. Cu₈Sn,	81·15	18·85	18·88	18·56	24·6	Like No. 9.
12. Cu₁₀Sn,	84·33	15·67	15·18	15·18	{ 20·06 24·50	Distinctly yellow.
13. Cu₁₅Sn,	89·00	11·00	—	—	13·1	Gun-metal.

Bronze may be considered as an alloy of copper and tin, but lead, zinc, nickel, phosphorus, manganese, iron, silicon, or other elements are sometimes added to produce certain effects

or to reduce the cost. Zinc in small quantity is beneficent but makes bronze harder. Iron and manganese harden it, and, when in small quantities, increase the tenacity. Phosphorus and silicon act as deoxidisers and produce hard, tenacious, and close-grained alloys. Phosphorus increases the electrical resistance more than silicon. Very small quantities of sulphur, arsenic, and antimony render bronze brittle, ·1 per cent. being sufficient to modify its properties.

The physical properties of bronze depend upon the composition, mode of manufacture, mechanical treatment, and rate of cooling after heating. Riche has examined a series of copper-tin alloys with regard to fusibility, liquation, and changes of density resulting from certain operations.* The alloys having the chemical formulæ $SnCu_3$ and $SnCu_4$, are the only ones which melt and solidify without decomposition, and their melting points lie between 600° and 700° C.; all other alloys of tin and copper undergo liquation at the moment of solidification.

The several alloys, in quantities of 500 to 700 grammes, were fused for ten hours in tubular moulds, and the top and bottom portions of the castings were analysed. Another portion of each of the melted alloys were stirred during solidification, and the portion which last remained fluid was poured off and likewise analysed. The preceding table (p. 60) gives the results.

The specific gravity of these alloys is best determined by filing off portions from the upper and lower ends of the casting, and taking the mean of the two densities. In alloys rich in tin expansion takes place (that is to say, the specific gravity of the alloy is less than the mean specific gravities of the two metals) up to the proportion $CuSn_2$; alloys richer in copper exhibit contraction, which is small in the alloy $SnCu_2$, then suddenly becomes very great, attains its maximum in $SnCu_3$, and then gradually diminishes, the greatest density, 8·91, is found in the alloy $SnCu_3$.

The hardness of the alloys, reckoning from pure tin, increases with the proportion of copper down to CuSn. This and all the more cupriferous alloys down to Cu_5Sn are extremely brittle, and from this alloy the hardness diminishes as the proportion of copper increases. The hardness of the alloy consisting of 66·66 parts tin and 33·33 parts copper is said to be the same as that of pure copper. The alloy $SnCu_3$ is distinguished from all the rest by several characters; it

* *Ann. Chem. Phys.* (4), Vol. XXX., p. 351.

presents the same homogeneous composition after repeated fusion, is peculiar in colour, has the highest density, exhibits the greatest degree of contraction, and is so brittle that it may be pounded in a mortar.

Gun Metal contains 8 to 11 per cent. tin, and the rest copper, but it is frequently made with more zinc than tin. *Bell Metal* contains 76 to 80 per cent. copper, and 24 to 20 per cent. tin. Small bells are often made of brass. *Speculum Metal*, containing 68 to 70 per cent. of copper and 32 to 30 per cent. tin, is white, admits of a beautiful polish, and was formerly much used for mirrors.

Aluminium Bronzes are alloys of copper and aluminium made by melting copper and adding aluminium, of which the 10 per cent. aluminium alloy is the strongest. It has a gold colour, takes a high polish, is very hard and malleable (best rolled very hot), and has a tenacity of 48 tons per square inch. The addition of 2 to 3 per cent. of brass increases its tenacity, and renders it less liable to oxidation. The 5 per cent. alloy is less hard than the above, and has the colour of pale gold. Aluminium brass contains 2 parts copper, 1 part zinc, and about 2 per cent. of aluminium.

Manganese Bronze is brass to which 2 or 3 per cent. of manganese has been added. The manganese in ordinary manganese bronze is added in the shape of ferro-manganese. This necessarily adds to the mixture about 15 lbs. of iron for every 85 lbs. of manganese; this iron is undoubtedly injurious. Cowles' manganese bronze is made by smelting together, in the electric furnace, lake copper and chemically pure black oxide of manganese (artificially refined); the result is a high grade copper-manganese alloy.

Nickel Alloys.—German silver is perhaps the most important alloy of nickel, and consists essentially of nickel, copper, and zinc. Different names are used to signify the same substance, such as : *Nickel-Silver, Argentan, Packfong, White-Copper, Weisskupfer, Neu-Silver,* and *Maillechort.* Besides these, different manufacturers employ fanciful names to denote alloys containing different proportions of the constituent metals, which they consider best suited to produce a given result, a good white colour being a great desideratum. Thus *Nevada Silver, Virginia Silver, Potosi Silver, Silveroid, Silverite, Electrum, Afénide, Argiroide,* etc., are simply German silver, but in some cases a little cobalt is present as well as nickel, and some makers add a small quantity of iron or manganese. 1 to 3 per cent. of lead is sometimes added for cast work.

The properties which make German silver so valuable are:
—its white colour, lustre, hardness, tenacity, toughness,
malleability, ductility, and power of resisting certain chemical
influences. When carefully prepared it works well under the
stamp and between the rolls, but it is advisable that the
metals used in alloying should be as pure as possible, since
small quantities of certain impurities, such as arsenic,
seriously injure its working qualities. Cobalt frequently
accompanies nickel in its ores, and becomes reduced at the
same time as that metal, and alloys readily with it; but as
the properties of both metals are similar, cobalt does not
greatly injure nickel for making German silver.

The following proportions make good malleable alloys:

Copper, . .	52	54	54	56	58	60	60
Nickel, . .	20	18	16	14	12	10	8
Zinc, . .	28	28	30	30	30	30	32

German silver is made in crucibles by melting the requisite
proportion of a 50 per cent. cupro-nickel alloy and adding the
requisite zinc in the form of brass containing equal parts of
copper and zinc. Cupro-nickel containing 75 parts copper
and 25 parts nickel is used for small coins, and an alloy of
80 parts copper and 20 parts nickel is employed for projec-
tiles.

Lead Alloys.—Alloys containing 75 to 80 per cent. lead
and 25 to 20 per cent. antimony are used as white metal for
bearings.

Type Metal contains 70 to 80 per cent. lead, 15 to 20 per
cent. antimony, and 5 to 10 per cent. tin.

Shot Metal is lead with ·2 to ·3 per cent. arsenic, which
causes small fragments of molten metal to assume the
globular form in falling from a considerable height.

Pewter contains about 80 parts tin and 20 parts lead, but
small quantities of copper, zinc, or antimony are sometimes
added.

Soft Solders are alloys of lead and tin, and to a certain
extent the fusibility diminishes with the increase of tin up
to 65 per cent. The alloy, having the composition 65·3 tin
and 34·7 lead, has a lower melting point than tin or any other
alloy of lead and tin. Metallic tin is sometimes used alone,
as in soldering fine utensils of tin plate. Lead is also soldered
to lead by simply melting the edges by means of a blowpipe

flame, as in the case of lead sheets for lining sulphuric acid chambers. This is termed *autogenous soldering.*

Soft solders are termed *common, medium,* or *best,* according to the amount of tin, those containing most lead being the cheapest. Fine or best solder is largely used for Britannia metal, best tin-plate, brass, and other metal articles. The commoner varieties are used by plumbers. An alloy of 1 part tin to 2 parts lead is termed "plumbers' sealed solder," and stamped by the "Plumbers' Company."

The following table gives the proportions employed for different kinds of soft solder.

Tin.	Lead.	Tin.	Lead.
1	10	1½	1
1	5	2	1
1	3	3	1
1	2	4	1
1	1	5	1

The quality of the solder is roughly judged by the appearance of the surface after being cast into a mould and allowed to cool. With excess of lead, the surface shows a uniformly grayish-white colour. With excess of tin, the surface is bright with dull grayish-white spots; in fact, the appearance approximates to that of lead or tin according to the amount of lead or tin present.

Fusible Alloys.—These consist chiefly of lead, tin, and bismuth. Newton's alloy contains 8 parts bismuth, 3 parts tin, and 5 parts lead, and fuses at 95° C. Rose's alloy contains 2 parts bismuth, 1 part tin, and 1 part lead, and fuses at 100° C. Wood's alloy contains 5 parts bismuth, 2 parts tin, 4 parts lead, and 2 parts cadmium, and fuses at 70° C.

Antimony Alloys.—*Britannia Metal* has a variable composition, but the following may be taken as a type :—90 parts tin, 8 parts antimony, and 2 parts copper. *Regulus of Venus* is a violet-coloured alloy containing 50 parts copper and 50 parts antimony. The effect of even small quantities of antimony on malleable metals is generally injurious, tending to make them hard and brittle.

Gold Alloys.—Silver and copper are the metals generally used to alloy with gold. They harden it, make it stronger, more fusible, and modify its colour. Pure gold is commonly

expressed as fine gold or 24 carat fine, the pound or 1000 parts being divided into 24 equal parts. Thus, 22-carat gold signifies that in 24 parts there are 22 parts gold and 2 parts of other metals. 9-carat gold likewise contains $\frac{9}{24}$ gold and $\frac{15}{24}$ other metals. The metal or metals added to gold are technically termed the alloy.

The following proportions as given by Gee are used for jewellers' alloys :

Carat.	Copper.	Silver.	Gold.
23	$\frac{1}{2}$	$\frac{1}{2}$	23
22	1	1	22
20	2	2	20
18	3	3	18
15	6	3	15
13	8	3	13
12	$8\frac{1}{2}$	$3\frac{1}{2}$	12
10	10	4	10
9	$10\frac{1}{2}$	$4\frac{1}{2}$	9
8	$10\frac{1}{2}$	$5\frac{1}{2}$	8
7	9	8	7

Different shades of colour in gold alloys are produced by different metals. An alloy of 18 parts gold and 6 parts copper has a reddish colour ; 18 parts gold and 6 parts silver has a green tint ; 18 parts gold and 6 parts iron has a bluish tint.

The British standard for gold coins is 22 carat, or 916·666 parts of gold and 83·333 parts of copper per thousand. *Gold solders* are alloys of gold, silver, and copper, having a lower melting point than the article to be soldered. The following among others are used :

Description.	Fine gold.	Fine silver.	Copper.
Best solder, .	$12\frac{1}{2}$ parts.	$4\frac{1}{2}$ parts.	3 parts.
Medium solder, .	10 ,,	6 ,,	4 ,,
Common solder, .	8 ,,	$6\frac{1}{2}$,,	5 ,,

These solders may be rolled thin, cut with the shears, and pressed into suitable pieces termed "pallions," or filed into dust, according to the needs of the workman.

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Arsenic, antimony, and lead are very injurious to gold, even when present in minute quantities. Aluminium and gold alloy well together. Roberts-Austen states that gold with 10 per cent. of aluminium is white; but when the aluminium is increased to 22 per cent., a ruby-coloured alloy having the formula $AuAl_2$ is formed.

Silver Alloys.—Silver and copper unite in all proportions, forming alloys nearly as malleable and ductile as silver, but possessing greater hardness, elasticity, and sonorousness. The colour is white until the copper reaches nearly 50 per cent., but beyond that the colour gets gradually yellower, and when the copper reaches 70 per cent. a reddish tint prevails. The hardest alloy is that containing 5 parts by weight of silver and 10 to 11 parts of copper. The alloy containing 630·29 parts of silver per 1000, and represented by the formula AgCu, has a lower melting point than silver, or than that of any other alloy of silver and copper. The alloy containing 718·93 parts of silver per 1000 is termed Levol's homogeneous alloy. Most of the other alloys of copper and silver undergo liquation on cooling from the molten state. *Standard silver*, as used for the British coinage, contains 925 parts silver and 75 parts copper per 1000. *Silver solders*— The following are used : (1) 60 silver, 26 copper, and 14 zinc; (2) 64 silver, 24 copper, and 12 zinc ; (3) 67 silver, 23 copper, and 10 zinc. For commoner alloys more zinc is added to the solder and sometimes other metals, such as tin and arsenic.

Amalgams.—Mercury or quicksilver readily unites with other metals, forming what are termed amalgams, some of which are liquid, and others solid or semi-solid. The solid amalgams appear for the most part to consist of metals united in atomic proportions ; and the liquid amalgams to contain a compound dissolved in excess of mercury. Mercury in small quantity is useful in alloys required to have low melting points, as in the case of fusible alloys used for stopping teeth.

Mercury unites readily with lead, zinc, tin, bismuth, cadmium, copper, gold, silver, magnesium, potassium, and sodium. The following metals unite with mercury with difficulty : iron, nickel, cobalt, manganese, and platinum in the compact state.

An amalgam of tin, silver, gold, and mercury is used as a cement for teeth. 1 part gold and 3 parts silver are melted, and 1 part tin is added. The resulting alloy is pulverised when hot, and then well kneaded with an equal weight of mercury. Mercury has a great solvent action on gold, and

is capable of dissolving a considerable amount without losing its liquidity.   A piece of gold rubbed with mercury is immediately penetrated by it, and becomes exceedingly brittle.   Gold-amalgam dissolves in mercury, forming a liquid mass. When this solution is strained through chamois leather, mercury passes through, together with a small quantity of gold, and there remains a white amalgam of pasty consistence.

Silver and mercury unite slowly at ordinary temperatures, but much more quickly when heated.   The affinity of these metals for each other is nearly the same as that of mercury for gold, but with a greater tendency towards crystallisation.   The more finely divided the silver, the more rapidly does amalgamation take place.   By pressing the product in a chamois leather bag, the free mercury runs through and a soft white amalgam is left.

Sodium combines rapidly with mercury at ordinary temperatures, the combination being attended with a hissing noise and vivid combustion.   A piece of sodium thrown upon mercury is forcibly thrown out of the vessel, accompanied by an explosion, in consequence of the great heat produced.   Sodium-amalgam is also prepared by triturating the two metals together in a dry mortar, fitted with a cover, until the combustion ceases.   With 30 parts mercury to 1 of sodium, it is tolerably hard under the file, and exhibits a crystalline laminar fracture.   With 40 parts mercury to one of sodium the amalgam is still solid, but softer than the former.   With 60 parts mercury to 1 of sodium it forms a stiff paste at 21° C.   100 parts mercury to 1 of sodium produces a viscous mass ; and 128 parts mercury to 1 of sodium is liquid.

Sodium-amalgam is used in the preparation of other amalgams.   It has been used for the extraction of gold and silver from their ores instead of mercury.   It is said to facilitate the amalgamation, and to prevent *flouring* of the mercury ; *i.e.* it prevents the formation of oxide, sulphide, arsenide, etc., which would form a coating on the mercury and prevent contact with the gold or silver.

Iron Alloys.—In the following alloys the metals known as malleable iron, cast iron, and steel are considered simply as different varieties of iron.

Iron and Manganese.—Iron readily unites with manganese, and when the proportion of the latter metal is considerable, the alloy is very hard, whiter, more fusible, and much more brittle in character than iron.   In small quantity, up to ·4 or

·5 per cent., manganese is highly beneficial in steel, and some of the very best steel is that containing a little manganese. Steel containing from $2\frac{1}{2}$ to 7 per cent. of manganese is brittle and comparatively worthless ; but when the amount exceeds 7 per cent., alloys possessing very great strength and toughness are obtained.   A sample containing ·48 per cent. carbon and 4·9 per cent. manganese, though very ductile while hot, can be reduced to powder by a hand-hammer when cold, little or no cohesion seeming to exist between the particles.   On the other hand, a specimen of forged material, containing about 14 per cent. manganese and ·85 per cent. carbon, when water-toughened has a tensile strength of 60 tons per square inch, with 50 per cent. elongation.   This is the strongest alloy of manganese steel.   When manganese steel is plunged into water, no hardening effect takes place like that of ordinary steel, but the metal, with upwards of 7 per cent. manganese, acquires increased tenacity and tough- ness.   When the manganese exceeds 20 per cent. the alloy is non-magnetic.   Manganese steel does not exhibit the anoma- lous expansion and after-glow, termed " recalescence," which takes place in magnetic metals when they cool to a certain critical temperature from a white heat.

Iron and Nickel.—These metals unite in a great variety of proportions.   Nickel is found in meteorites alloyed with iron.   The presence of nickel, up to 7 per cent., in mild steel increases the elastic limit and breaking stress, but the extensibility is diminished.   Alloys with 8 to 15 per cent. are exceedingly hard and brittle.   This quality of hardness continues as the nickel is increased, until about 20 per cent. is reached, when a change takes place, and successive addi- tions of nickel tend to make the steel softer and more ductile. With regard to the hardening effect of nickel on iron, there is some resemblance to the manganese steel previously de- scribed.   The whole of the series of nickel steels up to 50 per cent. nickel take a good polish and finish, with a good surface, the colour being lighter with the increased additions of nickel.

Mr. Riley states that the steels rich in nickel are prac- tically non-corrodible, and that those poor in nickel are much less so than other steels in this respect.   The 1 per cent. nickel-steel welds fairly well, but this property deterio- rates with each addition of nickel.   Mr. Hall states that the alloys of nickel and iron are among the most powerful con- nected with the magnet that he has seen or heard of.   The conductivity for electricity of iron-nickel alloys is extremely

low, and the electric resistance extremely high. The alloys
of iron and nickel may be prepared by melting iron and
nickel together; by reducing oxide of nickel with carbon in
the presence of iron; or by adding ferro-manganese to molten
iron and nickel to obtain nickel steel.

Iron and Chromium.—These alloys are hard, brittle, and
crystalline. When only a very small quantity of chromium
is present in steel, the influence is very small. Ferro-chrome
is produced in crucibles, and a certain proportion of this
rich alloy is added to the steel. The usual specimens of
ferro-chrome contain from 42 to 52 per cent. of chromium.
The metal is cast into iron moulds and chilled. The following
table shows the composition per cent. of different samples;
and it is interesting to notice the large amount of carbon
taken up by the alloys:

		Per cent.						
Chromium, . .	80	66	52	42	25	18	16	12
Carbon,. . .	11	9·5	7·8	7·3	6·7	6·2	2·7	2

The remainder would be iron and silicon, the latter some-
times exceeding 2 per cent. The hardness and brittleness
increase with the proportion of carbon and silicon. When
ferro-chrome is cooled slowly it crystallises, forming a mass
of needle-shaped crystals, which are more apparent when
the carbon is low.

With regard to magnetism, chromium has a much less
powerful effect in destroying the magnetic properties of iron
than manganese, for iron containing 65 per cent. of chromium
is still attracted by a magnet.

In the manufacture of steel, varying proportions of chrom-
ium may be used. Brustlein states that steel containing 2
per cent. carbon and 12 per cent. chromium may be forged.
The presence of chromium in steel increases its tenacity and
imparts a higher resistance to pressure. It also renders steel
harder to file or work on the lathe in proportion to the
quantity of carbon present.

Iron and Tungsten.—Steel containing tungsten is highly
valued for cutting tools. Formerly, the oxide of tungsten
and carbon were melted in crucibles with Swedish or good
hematite pig iron. The steel is now made by introducing a
rich alloy, containing up to 50 per cent. of tungsten, into the
crucible or bath of metal. Tungsten steel is known in
England as Mushet's special steel. It possesses a natural
hardness of its own, and when upwards of 3 per cent. of
tungsten is present, instead of being hardened by heating

and quenching in water, like ordinary steel, it is actually softened. It is very difficult to forge, and cannot be welded when the tungsten exceeds 2 per cent., but can be cast into the form of tools, which can be ground to a fine edge. Tungsten gives to steel a very fine and uniformly crystalline structure, and such steel is less affected by the atmosphere than ordinary steel. Mr. Stroh states that tungsten steel possesses remarkable magnetic properties. He uses a 3 per cent. tungsten alloy for telephone magnets with marked advantage. Tungsten steel is very fragile under shock, and its extensibility is very low.

Iron and Copper.—Copper has been considered very injurious in iron and steel, and the injurious effects attributed to copper are very marked when sulphur is present in notable quantity, making the metal red-short. M. Choubly of the Firminy Steel Works has experimented on phosphoric steel containing copper, and he states that a metal containing ·5 per cent. of carbon, ·15 of phosphorus, ·04 of sulphur, and 1 of copper rolled perfectly well. Messrs. Ball and Wingham have investigated the influence of copper on the tensile strength of iron and steel. An alloy containing—

Copper, ...	7·550
Carbon, ...	2·720
Manganese, ...	·290
Silicon, ...	·036
Phosphorus, ...	·130
Sulphur, ...	·190

was bright, white in colour, crystalline, and very hard, but did not offer any great resistance to impact. Varying quantities of the alloy were melted down with Bessemer steel, and test pieces 1 inch by $\frac{1}{4}$ inch by $\frac{3}{10}$ inch were annealed and tested. The following table shows the results:

No.	Copper.	Carbon.	Tensile Strength.
1	·847	·102	18·3
2	2·124	·217	36·6
3	3·630	·380	47·6
4	7·171	·712	56·0

From these experiments the authors conclude that copper increases the tensile strength of iron. The simultaneous

presence of carbon assists in the more intimate association of copper with iron.

Iron and aluminium.—When much aluminium is present with iron, a series of hard, brittle, close-grained alloys result, termed "ferro-aluminium." When the aluminium exceeds about 17 per cent. the alloy becomes non-magnetic, like ferro-manganese. Aluminium added to molten iron and steel lowers their melting points, increases the fluidity of the metal, and causes it to run more easily into moulds, and to set solid without the formation of blowholes. Mr. Nordenfelt adds a small quantity of aluminium to wrought iron, which lowers the melting point sufficiently to enable it to be poured like ordinary cast iron. The effect of a small portion of aluminium on steel is to raise its elastic limit and ultimate strength, as well as to impart the properties mentioned above.

The effect of aluminium on cast iron has been studied by Mr. Keep of Michigan, who states that the appearance of the fracture is a strong indication of the character of the metal, and that a bar $\frac{1}{2}$ inch square, more than any other size, shows by a change in the grain the effect of varying composition. A smaller bar chills so quickly that it does not give an element sufficient time to exert its influence, while a larger bar holds its heat so long that any tendency towards a white grain is more or less overcome. He commenced his tests with a pig-iron containing 1·27 graphite, 1·71 combined carbon, and ·08 silicon, which gave castings full of blowholes. To a portion of this pig-iron ferro-aluminium was added, so as to produce a metal containing ·25 aluminium, 1·37 graphite, and ·2 silicon per cent. The result was a more even grain, with absolutely no blowholes. The silicon had increased and added to the hardness of the casting.

The following are the proportions of aluminium generally used for iron and steel:

For Bessemer steel, . .	0·2 per cent.
„ Martin steel, . .	0·05 per cent.
„ Crucible steel, . .	0·10 per cent.
„ Cast iron, . . .	0·1 to 0·2 per cent.

These proportions may be varied to suit particular cases, but in order to obtain the best results, it does not seem advisable to greatly exceed the maximum of 0·2 per cent. The molten iron should be run from the cupola into the ladle;

then the right proportion of aluminium added by means of a pair of tongs, or better, in an iron cartridge, or cylinder, fixed to an iron rod, and provided with many holes through the side, to allow the molten aluminium to escape. It should be plunged sharply through the fluid metal to the bottom of the ladle, and stirred thoroughly for at least two minutes. On the introduction of the aluminium, the mixture will be found to become very lively and to work considerably, almost, so to speak, to boil ; the stirring should be continued until this agitation begins to subside. If the mixture is not well stirred, the castings will be spongy and have little air cells in them. Both the tongs (or cartridge) and the aluminium should be heated and dried before plunging, or the metal may fly. The aluminium may, however, be dipped in benzine previous to use. The workmen carrying out the operation should wear goggles, and be otherwise well guarded against the metal flying. If it is desired to add the aluminium in the form of a rich alloy, these alloys may be purchased, or any given alloy can be readily made by following out the above instructions.*

* For fuller information concerning Alloys see Hiorns' *Mixed Metals* (Macmillan & Co.).

CHAPTER V.

FLUXES, SILICATES, AND REFRACTORY MATERIALS.

A FLUX is a substance added to metalliferous matter in order to unite with extraneous matter and remove it, generally in the form of a fusible slag. It varies with the nature of the bodies to be removed. If such bodies are of an acid nature, such as silica, the flux must be basic or neutral. If, on the other hand, a basic substance has to be removed, an acid flux is generally required. In many cases of the simple melting of metals, an oxidising flux is added to oxidise the impurities, in which state they readily combine with an acid flux to form a liquid slag, or volatilise, or simply rise to the surface as a dross. The following are the fluxes most commonly used.

1. Siliceous materials, such as sand, quartz, and natural silicates, are used for fluxing basic materials, in steel and copper furnaces.

2. Calcareous materials, such as limestone, dolomite, and the same after calcination, are used as fluxes for silica, silicates, and acid materials, such as phosphoric acid, in iron and steel making processes.

3. Aluminous materials, such as clayslate, are sometimes used as a flux for lime.

4. Fluorspar is valuable for fluxing sulphates of baryta, lime, strontia, lead, etc., also phosphate of lime. At a high temperature it melts into a transparent liquid. It is partly decomposed by silica, with the liberation of the gas silicon-fluoride, but the greater part unites with the silicate formed, which it renders more fusible and increases its fluidity when melted.

5. Sulphides and sulphates are useful as sulphurising agents. Barium sulphate is used to yield sulphur to nickel

in nickel ores and slags, and iron pyrites is used for the same purpose in copper smelting ; baryta and oxide of iron, being powerful bases, readily unite with silica and form a fusible slag, leaving copper and nickel as a regulus. Iron pyrites also renders zinc sulphide fusible.

6. Alkaline fluxes are chiefly used in refining metals and seldom in large operations. Certain chlorides are employed. Ammonium chloride is used as a source of chlorine in purifying gold. Common salt is a flux for silica, it is fusible and serves as a protecting covering to molten metals. It also moderates the action of bodies which cause violent ebullition. Borax is a good flux for silica as well as for bases, sulphides, and arsenides. Sodium carbonate is an oxidiser to many metals, and therefore a desulphuriser. It forms readily fusible compounds with silica and many oxides. It also acts as a reducing agent in the case of silver chloride. Potassium cyanide is an excellent flux for sulphur, as well as for silica and other infusible bodies.

Choice of Fluxes.—When the gangue of an ore is basic, such as lime, alumina, dolomite, oxide of iron, etc., a siliceous flux is added. If the gangue contains a single base then a silicate is added so as to form a silicate with a double base, which is more fusible than a silicate with a single base. If the gangue consists of clay, as in clay ironstone, then a single base such as a lime is best to be added as the flux. If the gangue contains two or more bases then a flux of silica alone is required.

Calculation of Fluxes.—The quantity of flux required for a given gangue will vary with the nature, as well as with the amount of gangue to be removed. Take the case of a blast furnace slag, which is a monosilicate, containing $2Al_2O_3$, $3SiO_2 + (2MO.SiO_2)$ where M may be lime and magnesia, and suppose the ore to be smelted is oxide of iron associated with clay containing an excess of silica. Now the gangue of the ore and the ash of the fuel may contain for example 8 per cent. of alumina, 4 per cent. of magnesia, 7 per cent. of lime, and 20 per cent. of silica.

$$2Al_2O_3.3SiO_2 = 204 + 180 = 384.$$
$$2MgO.SiO_2 = 80 + 60 = 140.$$
$$2CaO.SiO_2 = 112 + 60 = 172.$$

Now 204 Al_2O_3 requires 180 SiO_2 ∴ 8 will require **7·06**
  „ 80 MgO „ 60 „ ∴ 4 „ „ **3·00**
  „ 112 CaO „ 60 „ ∴ 7 „ „ **3·75**
                                        13·81

13·81 parts of silica are therefore satisfied, leaving 6·19 parts to be fluxed off. If lime be the flux, as is usual, then by the above proportion 60 parts of SiO_2 require 112 parts of CaO, therefore 6·19 will require 11·55 parts of CaO to be added. The following graphic method of determining the proportion of flux to be added is given by Balling (Fig. 17). The dark line represents the proportion of silica to alumina as given in the above formula ; and the thin lines the proportion of silica to lime and the proportion of silica to magnesia. To determine the amounts given in the above calculation, draw
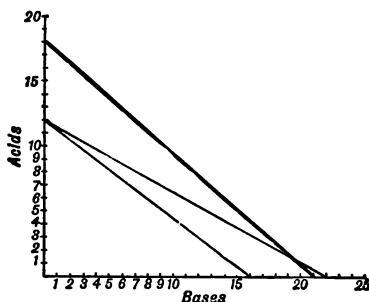
Fig. 17.

lines parallel to the given lines from the acid line to the base line for each metallic oxide, and the reverse if the silica is required, and where they cut the horizontal and vertical line respectively the amount of base or acid to be added as a flux will be indicated. Thus, for alumina, a line drawn from 8 on the base parallel to the dark line will cut the vertical at 7·06 ; or a line from 6·19 on the vertical drawn parallel to the upper thin line will cut the base at 11·55, which is the amount of lime required in the above calculation.

Slags.—A slag may generally be considered the waste product of a metallurgical operation. It is usually a multiple silicate. The difference between a slag and a scoria has been already briefly explained in defining metallurgical terms. The bases most often found in slags from smelting ores are lime, magnesia, alumina, and oxide of iron, with small quantities of alkalies and the metals whose ores are being smelted. Both the silica and bases are derived from the earthy matter of the ore, the ashes of the fuel, the flux,

and the material of which the furnaces or crucibles are con-
structed. In melting and refining metals they are partially
oxidised, and the slag largely consists of these oxides, which
are often re-smelted to recover the contained metals. The
slags most frequently produced are those with an iron base,
of which the most fusible is the protosilicate ($2FeO.SiO_2$).
It has a dark olive green to black colour, is opaque and but
slightly crystalline. Manganese sometimes partially replaces
the iron. Oxide of zinc forms with silica practically in-
fusible silicates, and as a rule the presence of this oxide
diminishes the fusibility of silicates of iron, lime, etc. Zinc
oxide and alumina not only interfere with the fluidity of the
slag, but also cause a scum to form, which is difficult to
separate from the slag. Protoxide of tin augments the
fusibility of multiple silicates. The proto- and bi-silicates of
copper melt easily ; they augment the fusibility of earthy
silicates. Oxide of copper is easily separated, especially in
the presence of sulphur or arsenic, with which it forms
regulus or speise respectively. The oxides of lead and bis-
muth are, next to the alkalies, the most fluxing bases.
Silicates of lead melt at a red heat. Oxide of lead increases
the fusibility of multiple silicates, but it is easily reduced by
the presence of metallic iron.

Slags are either vitreous or stony, and not infrequently
they are more or less crystalline. Rapid cooling tends to
produce the glassy variety, and by slow cooling the crystal-
line structure is induced. The stony condition is prevalent
in slags in which earthy bases predominate. The object in
forming slags in melting metals is to form readily fusible
compounds, which shall contain the impurities it is desirable
to remove, and at the same time be as free as possible from
the metal or metalliferous substance undergoing preparation.
When the slag is the waste product of an operation and is
free from useful metals, it is said to be clean. It frequently
happens that the slags produced in dealing with a given
kind of metalliferous matter are useful as a flux or other
agent in extracting or melting different metals.

When the charge is improperly prepared, and either silica
or lime predominate, or when the amount of alumina or
magnesia is very large or the temperature insufficient, the
slags are imperfectly melted, and present a kind of granular
fracture.

A slag consists of two portions, the acid, such as silica,
SiO_2, and the base, such as alumina, Al_2O_3. But alumina
may act the part of an acid when combined with a base

stronger than itself, as in the natural mineral, Spinel, $ZnO.Al_2O_3$. The former is termed a silicate and the latter an aluminate. Silicates may be classified as follows, according to the oxygen ratio of base to acid :

Subsilicates, . .	4MO,	SiO_2 or $4M_2O_3$, $3SiO_2$.
Monosilicates,. .	2MO,	SiO_2 or $2M_2O_3$, $3SiO_2$.
Bisilicates, . .	MO,	SiO_2 or M_2O_3, $3SiO_2$.
Trisilicates, . .	2MO, $3SiO_2$ or $2M_2O_3$, $9SiO_2$.
Sesquesilicates, .	4MO, $3SiO_2$ or $4M_2O_3$, $9SiO_2$.

The first column contains bases of the protoxide type, such as FeO and CaO. The second column contains bases of the sesqueoxide type, such as Al_2O_3.

Slags are economised in a variety of ways. Lead slags, for example, are used in smelting dirt and refuse containing precious metals. In copper smelting the slags are used as a flux. Iron slags are used for building purposes and for making and repairing roads. Slag from the iron blast furnace when mixed with $\frac{1}{10}$th its amount of lime makes a good hydraulic cement. When a jet of steam is blown through a stream of molten slag from an iron blast furnace a wool-like mass is obtained, known as slag-wool, which being a non-conductor of heat and fire-proof is used as a cheap substitute for asbestos. The slags obtained in copper and lead smelting are used respectively as a lining for the bottoms of the furnaces. In the basic process for steel the slag contains a considerable quantity of phosphate of lime, and is used as a manure for certain soils

REFRACTORY MATERIALS.

For smelting metals a furnace is required, built of, or at least lined inside with, a material capable of withstanding high temperatures without fusing, or softening, or decomposing by the heat to which it is subjected. As a rule the exterior is constructed of ordinary masonry, but the interior is lined with refractory material, the nature of which depends to a great extent upon the character of the operation to be performed. Refractory materials are either used in the natural state, such as silica, alumina, oxide of iron, magnesia, and fire-clay ; or they undergo a preliminary preparation before use. In some cases the materials are moulded to the internal shape of the furnace. If they are not of a plastic nature like fire-clay, then clay, tar, or other binding material

is intimately incorporated with them, in order to impart the necessary plasticity.

Quartz or Silica.—This substance neither softens nor melts at the highest furnace temperatures, and is therefore a valuable material for internal construction, either when mixed with refractory clay to form silica bricks, or when used alone as a lining for the beds of reverberatory furnaces. Sand is not composed of pure silica, but the small quantities of lime, oxide of iron, and clay usually present are not objectionable. Dinas rock is a highly refractory substance, occurring in the Vale of Neath, and contains about 97 per cent. of silica, the remainder being lime, oxide of iron, alumina, alkali, and water. From this material, when mixed with 1 to 3 per cent. of lime, bricks are made, which form valuable linings for the roofs of many reverberatory furnaces.

Alumina is quite as infusible as silica, but is rarely found in nature in any great quantity in the pure state. Bauxite is perhaps the most useful, although it often contains large amounts of iron oxide and other impurities. It consists of about 3 to 5 per cent. of silica, about 25 per cent. of iron oxide, 50 to 60 per cent. of alumina, and 10 to 15 per cent. of water. It has a dark red colour, but sometimes it is found with very little iron, when it is white.

Lime and Magnesia.—These are infusible bodies, strongly basic in character, but they form fusible compounds with silica and other acid bodies. This property is utilised in steel furnaces, the interior of which is lined with these oxides, which unite with phosphoric acid, forming stable phosphates. Lime and magnesia occur in dolomite, from which material, after calcination, basic bricks are prepared.

Fire-clay.—The refractory bodies already referred to may be combined together in certain proportions, without ceasing to be refractory. Fire-clay is a hydrated silicate of alumina with varying amounts of lime, magnesia, oxide of iron, alkali, etc., and some mechanically mixed silica. The plastic property which clays possess is due to the chemically combined water. In all cases the plasticity disappears when the clay has been baked, and it remains granular and powdery. The clays of the coal-measures, such as those of Stourbridge, are admirably adapted for making fire-bricks, although not pliant enough for pottery. In fact an excess of plasticity is a disadvantage for metallurgical purposes, as the bricks would crack at the time of baking.

Ganister is a highly siliceous clay with sufficient plasticity to enable it to be used as a lining for furnaces. It is used for lining the acid Bessemer converter.

Crucibles, etc.—Earthen crucibles are made of fire-clay mixed with sand, burnt clay, or other infusible matter, so as to counteract the tendency which raw clay possesses of shrinking when heated. The bodies thus mixed with the clay expand, or do not contract on heating, having been already shrunk when burnt, and therefore act in an opposite manner to the clay. Such a composition must be able to resist a high temperature without softening, must not be friable when hot, and be capable of withstanding sudden changes of temperature without cracking, as when a white-hot crucible is brought out of a furnace into cold air.

Some crucibles are required to resist the corrosive action of metallic oxides in the material operated upon, and in the ashes of the fuel, so that a crucible should be selected which is best adapted to the special purpose to which it is to be applied.

The component parts of a crucible are first crushed to a fine powder, and passed through a sieve, the fineness of whose meshes will vary with the desired fineness of the grain in the pot, the plasticity being closely connected with the fineness of the particles—at any rate for small crucibles this closeness of grain appears to be indispensable; then the fine powder is mixed with water and kneaded to the right consistence for use. The best results are obtained by using a mixture of different fire-clays, the most infusible being those containing the largest amount of silica and the minimum of oxides of iron and lime. The presence of potash and soda in small quantities sensibly increases the fusibility, but they act advantageously in soldering the particles together. Iron pyrites, which is frequently disseminated through clays, especially those from the coal measures, is perhaps the most injurious constituent. A crucible made from such clay will become indented with small cavities, and even holes, when exposed to a prolonged high temperature. It follows then that the most refractory crucibles are those made from pure clays, the nearest approach to which is presented by some French clays.

The fitness of a clay for making crucibles may be determined by moulding a portion into the shape of a prism, or any form containing sharp edges, carefully drying, baking, and exposing to a high temperature in a covered crucible for

some time. If very refractory, the test-piece will show no signs of fusion. If the edges are rounded it is a proof of incipient fusion, and if melted, the clay is useless.

Clay vessels of all kinds may be tested to ascertain their power of resisting corrosion by melting in them a mixture of litharge, red oxide of copper, and borax, and noticing the time this mixture will take to permeate them. Those which resist this destructive action the longest will of course be the best. Many crucibles are by this means eaten away irregularly, showing the necessity of uniformity of grain to resist perforation.

All crucibles should be cautiously annealed before use by placing them in an inverted position over the furnace, otherwise they are liable to split when plunged into a red-hot fire. This tendency is noticeable even with the best plumbago crucibles.

Plumbago or black-lead pots are made from varying proportions of fire-clay mixed with powdered graphite or coke dust. Good graphite is neither altered nor fused by exposure to the highest temperatures (air being absent), so that it is an admirable substance for crucibles. The graphite is powdered, sifted, and mixed with sufficient clay to render it plastic. Good plumbago crucibles, after a careful preliminary annealing, withstand the greatest changes of temperature without cracking, and may be heated many times in succession.

When an ordinary crucible requires to be protected from the corrosive action of metallic oxides, or when small amounts of metallic compounds have to be reduced, the inside is coated with a lining of charcoal. This is done by first mixing the charcoal with sufficient starch, paste, or treacle to make it adhere when pressed. The crucible is then loosely filled with the brasque, and a cavity of the desired size made by boring with a triangular-shaped piece of wood, and then made smooth with a round elongated wooden tool, whose size and shape is apportioned to the capacity of the cavity desired, or the brasque may be plastered on the inside of the crucible by the hand.

Fire-bricks.—A fire-brick used to withstand high temperatures must only contain small quantities of the alkalies, which should not exceed 1 per cent. Glenboig, Stourbridge, and Wortley (Leeds) are the leading brands extensively used ; these are safe, though of course there are many other fairly serviceable bricks made of brands less in repute.

Ganister bricks are exceedingly valuable for withstanding the very highest temperatures for the crowns of reverberatory furnaces. They do not crack on cooling so much as bricks composed almost entirely of silica. The *Lowood* brick, made near Sheffield, has a very high reputation in this class. Ganister bricks should be set in thin ganister cement. Crowns are best put on dry, and just "slurried" over the top when finished. No fire-brick has a fair chance if set in a clay inferior to itself; but however good the clay, the best furnace builder will use as little as possible.

Dinas bricks are practically infusible, and composed almost wholly of silica. The fractured surface presents a coarse, irregular structure of a light-brown colour. The lime which is added exerts a fluxing action on the particles of quartz, and so causes them to agglutinate.

The following analysis will serve to show the composition of British materials used in furnace construction :—

	Silica.	Alumina.	Ferric oxide.	Lime.	Magnesia.	Potash and soda.	Titanic acid.
Fire-brick, Glenboig, . .	64·41	30·55	1·70	·69	·64	·55	1·33
„ Stourbridge, .	73·05	22·40	2·43	·39	·54	1·09	..
„ „ .	77·63	19·48	1·29	·18	·31	·91	..
„ Newcastle, .	73·30	20·56	1·69	1·55	·72	2·20	..
„ „ .	58·00	36·50	1·67	·58	·82	2·42	..
„ Pensher, . .	65·10	30·03	2·00	·45	·51	2·04	..
„ Flintshire, .	88·10	4·50	6·10	1·2	..	..	..
„ Leeds, . .	77·30	19·17	1·43	·45	·63	1·10	..
„ „ . .	72·65	23·75	1·75	·30	·36	·90	..
„ „ . .	67·82	25·56	2·00	1·12	·72	2·47	..
„ Elland, . .	62·33	35·59	1·25	·73	·10	..	..
Ganister bricks, Lowood, .	96·32	·99	·71	1·28	·25	·26	..
„ „ Witton, .	94·54	·89	1·10	2·85	·32	·30	..
Dinas bricks, Wales, . .	95·76	·42	·83	2·96	·26	·26	..
						Manganous oxide.	
Burnt Dolomite, Raisby Hill,	5·60	2·35	1·70	56·96	32·18	1·2	..
Ganister, Lowood, . .	89·55	4·85	1·28	..	·80	3·52	..
„ Weardale, . .	87·53	9·10	·64	·73	·40	1·55	..

CHAPTER VI.

FURNACES.

A HEARTH forge or furnace is an arrangement for con-
ducting metallurgical operations by the agency of heat.
The inside is generally lined with refractory material, and
the outside constructed of ordinary material. All fur-
naces may be divided into three classes : (1) those with-
out an independent fireplace, such as a blast furnace, and a
hearth ; (2) those with an independent fireplace, such as a
reverberatory furnace ; (3) those in which the material is
separated both from the fuel and from the products of com-
bustion, such as a zinc retort. They may be used with a
natural draught, the air being aspirated by means of a
chimney, or the air may be forced in by means of a blowing
apparatus. In both cases the heat developed depends on the
calorific power and weight of fuel burnt in a given time,
also on the mode of combustion, for if the combustion is
complete the whole of the heat may be utilised. Furnaces
may be classified thus :

Hearth.—The smith's hearth may be taken as a type of
this class, but some hearths, such as a lime kiln and that
used for liquation, are worked by means of a natural current
of air.

Shaft Furnaces.—These generally go by the name of
blast furnaces, of which those used for smelting iron ores are
typical. The vertical kilns for roasting iron ores have no
artificial blast.

Reverberatory Furnaces.—In this class the fire is
separated from the metalliferous matter by a low brick wall
termed a fire-bridge. They are generally worked by means
of a natural draught, but an air blast is sometimes used.

Closed Vessel Furnaces.—The vessel may be a cru-
cible, as in melting platinum ; or a retort, as in distilling

zinc ; or a tube, as in liquating bismuth ; or a more or less rectangular chest, as in the cementation of steel.

A *Hearth* is a low furnace in which the material to be operated upon is mixed with the fuel and flux. The heaps, stalls, and certain kilns for roasting ore are included under this title, as the fuel and ore are mixed, and the action is the same.

A *Shaft Furnace* contains one common receptacle for the materials used. The nature of the ore and fuel employed in a shaft blast furnace will determine the shape. In roasting iron ores, for example, where a large mass of material has to be expeditiously treated, and where only a moderate temperature is needed, the diameter is greater in proportion to the height than in the reducing furnace, which has a height three to five times the greatest width, because it is essential to have a high temperature in the region where the fuel is largely consumed, and the more fuel there is burnt in a given space in a given time the higher will be the temperature. Compare Figs. 37 and 43. The fuel employed is coal, coke, and charcoal, because oxides or materials which have been more or less oxidised by a previous roasting, are generally treated in the furnace. In the case of raw coal, it is decomposed by the heat in the upper portions of the furnace, so that by the time it reaches the zone of combustion it is in the form of coke. The carbon is first burnt to carbon dioxide by the action of the blast, but this, coming immediately in contact with highly-heated carbon, is changed to carbonic oxide ($CO_2 + C = 2CO$). This is the chief agent in effecting the reduction of the metallic oxides. A shaft furnace, supplied with air by means of a forced blast, may be theoretically divided into three parts. (1) The upper portion is the region of partial reduction, without melting ; carbonic acid is removed from carbonates ; any matter of a volatile nature is driven off, and raw coal is largely coked. (2) The middle portion may, to a great extent, be considered neutral, because the carbon dioxide, formed by the complete reduction of the metallic oxides in the lower part of the furnace is an oxidising agent, and therefore neutralises the effect of carbon and the reducing gases. (3) The lower portion, where the temperature is highest, is completely reducing. Here the flux and earthy matters, etc., combine and form a fusible slag ; the reduced metal also becomes liquid, and unites with other elements which have been simultaneously reduced, and falls to the bottom of the furnace in virtue of its specific gravity ; the slag, being lighter, floats on the top. Gruner

classifies blast furnaces according to the ratio of the maxi-
mum diameter to the height, thus :

1. Squat furnaces, in which the height is less than or equal
to, three times the diameter, $\dfrac{H}{D} < 3$.   2. Ordinary furnaces,
in which the ratio $\dfrac{H}{D}$ varies between 3 and 4.   3. Elon-
gated furnaces, in which the ratio $\dfrac{H}{D}$ is greater than 4.

The amount of metal produced per day and the consumption
of fuel per ton depends on the nature of the ore, and the
ease with which it is reduced. Some American blast furnaces
have a capacity of 18,000 cubic feet, and produce 150 to 250
tons of iron per day, with the consumption of about 20 cwts.
of fuel per ton of iron. A modern English iron blast fur-
nace produces about 500 tons of iron per week, or 70 to 80
tons per day. They vary from 65 to 85 feet in height, 16
to 22 feet wide at the boshes, and 7 to 9 feet wide at the
hearth. The fuel consumed per ton of iron is about 20 to 22
cwts. Blast furnaces for lead of the Rachette type are
about 20 feet high, 6 feet 6 inches wide at the top, and 4
feet 6 inches at the bottom, and yield 20 to 40 tons per day.
Some of these furnaces are rectangular in section (see Fig. 46).

Reverberatory furnaces are distinguished from the preced-
ing types in being what has been termed "vat" shaped, and
having a separate fireplace, which may be an ordinary grate
for burning solid fuel, or a special chamber in which fuel is
burned so as to produce combustible gases, and termed a
gas-producer. That portion of the furnace where the
material is being treated has been conveniently termed the
laboratory ; it is separated from the fire, but not from the
flames, by a low wall, termed the fire-bridge, and generally at
the chimney end there is another wall, termed the flue-bridge.
The chimney is connected with the laboratory by a flue of
varying length, and more or less horizontal. The chimney
serves the two-fold purpose of producing the draught, which
is regulated by a damper, and of carrying off the gaseous
products. The height of the roof of the furnace is generally
small as compared with the extreme length and breadth, for
on it will depend whether the flames act directly or by
radiation on the material. The roof generally slopes from
fireplace to flue, so that the flame may be reverberated or
deflected on to the material. The size of a reverberatory
furnace is determined by the kind of material to be operated

upon and the temperature required. When ores are simply roasted, a moderate temperature only is required. The length of the laboratory may be five to six times that of the fireplace ; but when a high local temperature is desired, the ratio of fireplace to bed may be as 1 : 2, as in the case of a puddling furnace. The atmosphere of an ordinary reverberatory furnace is essentially oxidising, and is modified by the arrangement of the fire on the bars of the grate. If the fuel is kept in a thick layer much carbonic oxide will be produced, which is a reducing gas ; but if the layer of fuel is thin, much of the air can readily penetrate through, with little change, and the gas produced by the combustion of the fuel is then chiefly carbon dioxide, and the atmosphere is intensely oxidising. This, however, depends on the rapidity of the draught. The following table will show certain particulars of typical reverberatory furnaces :

Name.	Length and greatest width of bed.	Section of fireplace.	Amount of metalliferous material employed.	Fuel used.
Tin Smelting furnace, . . .	18 ft. × 9 ft.	2 ft. × 2 in.	24 cwts.	15 cwts.
Puddling furnace,	5 ft. 6 in. × 4 ft. 8 in.	3 ft. 9 in. sq.	4–5 cwts.	4–5 cwts.
Copper calciner, .	20 ft. × 12 ft.	4 ft. × 3 ft.	5–10 tons.	..
Copper furnace for regulus, . .	15 ft. × 10 ft.	5 ft. square.	30 cwts.	5 cwts.
Lead smelting furnace, . . .	12 ft. × 7 ft.	2 ft. 6 in. sq.	21 cwts.	12 cwts.
German cupellation furnace, .	8 to 10 ft. diameter.	4 ft. × 1 ft. 6 in.	5–15 tons.	..

An electric furnace manufactured by Ducretet & Lejeune, Paris, is shown Fig. 18. The carbons CC' are oblique, and movable in their metallic mountings GG'. They are easily brought in contact or separated. The whole forms a closed space, with refractory walls R receiving the movable crucible Cr. Pipes serve for the circulation of the gases and for the introduction of the substances to be submitted to the action of the electric arc. The phenomena of fusion and reduction can be directly observed. The walls of the apparatus consist of movable shutters K fitted with mica, which can be replaced by refractory plates. The hearth upon which the crucible is placed is regulated by the movable rod Re. According to the substances to be reduced, the crucible is made of carbon, magnesia, lime, etc., or of metal. The arc

between the two carbons CC′ is transformed into a lengthened flame in consequence of the directing action of a magnet A1 placed near the apparatus. The arc can thus be directed on to the material contained in the crucible and gradually be brought to the maximum temperature. This arrangement, the inventors say, is a new application of a phenomenon already utilised by Jamin in his electric lamp. The block of wood supporting the magnet can be omitted. It is sufficient
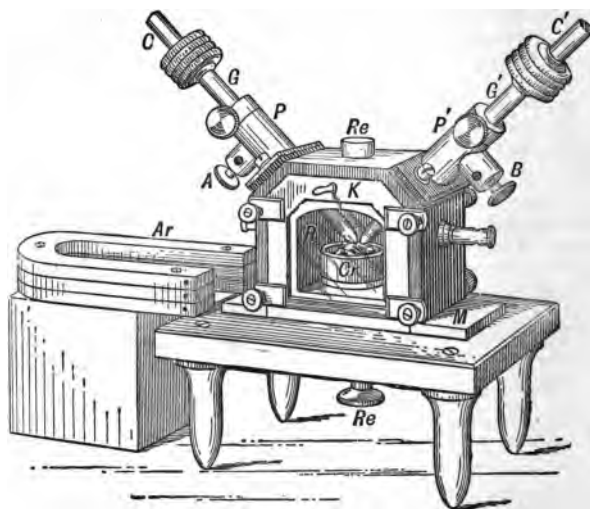
Fig. 18.

to give it an inclined position in allowing it to rest directly upon the table. The model as shown in the illustration can sustain, with carbons of suitable diameter, a current of 40 amperes. With a current of 12 amperes and 55 volts, the reduction of oxides and the fusion of the most refractory metals can be effected in more than sufficient quantity for their chemical or spectral analysis. Moissan with his electric furnace has succeeded in fusing lime, and in preparing such difficultly reducible metals as zirconium, chromium, and calcium. Recently, too, MM. Joly and Vèzes, of the Ecole Normale Supérieure, have brought to the metallic state,

with MM. Ducretet & Lejeune's crucible, without oxidation, ruthenium and osmium, by submitting them in a closed vessel, in presence of suitable gases, to the electric-arc temperature. In operations exposed to the air, notwithstanding the rapidity of fusion, the metal is invariably oxidised. With the oxyhydrogen blowpipe ruthenium oxidises in smelting, with a consequent sensible loss of metal. Osmium oxidises and vaporises as osmic acid. It is the same with all the difficultly fusible and easily oxidisable metals. The solubility of amorphous carbon in finished iron or liquefied cast-iron, and in other metals, is easily realised with the arc in a closed vessel, such as that shown in the above figure. It is advisable to have the interposition between the operator and the crucible of a large screen of smoked or ruby-red glass, or glass of various colours superposed, giving a neutral tint. These screens arrest a large portion of the luminous rays insupportable by the eye, and they obviate the hurtful calorific action on the skin. Plates of gelatine chloride of silver, with which all colours up to complete opacity can be obtained, form excellent screens, heating less than those mentioned above. The conductors of the crucible should only be handled by their insulated parts, in view of possible danger from contact with the continuous or alternating currents employed. A cut-off, introduced in the circuit near the apparatus, is recommended for strong currents.

NATURAL AND ARTIFICIAL DRAUGHTS.

Natural draught is obtained by means of a chimney. When gases and vapours escape from burning materials they are expanded and therefore tend to rise, because they are specifically lighter than the surrounding atmosphere, and would leave a partial vacuum if the place were not immediately filled with a supply of atmospheric air which is specifically heavier. Now, if a chimney be so tall that the upward currents of gases have time to cool until their density becomes greater than that of the external air, or even equal to it, then the practical limits of height have been exceeded. The pressure producing a current through the chimney is equal to the difference in the weight of a column of gas at the ordinary temperature, and of that of an equal column at the temperature of the chimney. The height therefore is regulated by the difference of temperature of the gases inside and outside the chimney, and the weight of such a column will decrease in direct proportion to the

rise in temperature, for gases expand $\frac{1}{273}$ of their bulk for every rise of 1° C. Now, the action of a chimney largely depends on the weight of air supplied in a given time; therefore there must be limit to its action, and this limit is stated to be reached when the difference of temperature between the external air and the internal gases is about 300°. For furnaces in which the combustion is very moderate the height need not exceed 35 feet ; for iron and copper refining furnaces about 50 feet is required ; and for steam boilers the chimneys are sometimes 60 to 100 feet high.

There is an intimate connection between the draught produced by a chimney and the size of the grate where the fuel is burned. If the grate is small, the draught will be keener for the same size of chimney than when the grate is of larger dimensions. If the draught is too slow, much carbonic oxide is formed ; but with a rapid draught the carbon is largely burnt to carbon dioxide ; if, however, the bed of fuel is deep, the temperature may become sufficiently high to form carbonic oxide by the reaction :—$CO_2 + C = 2CO$. Light, porous, and inflammable fuels, such as charcoal, form carbonic oxide more readily than coal and coke ; so that the latter are capable of being used with a greater depth on the grate than with wood and charcoal, without loss of heat by the formation of combustible gases and dust, which pass into the chimney.

Forced Draught.—The most primitive method is by means of bellows, made of the skins of animals, and having a spout for the delivery and admission of air. The skins were inflated by strings pulled by hand, and worked by the pressure of men's feet for the exhaust. Single-acting bellows with a valve were afterwards introduced, and these again were superseded by the double-acting bellows now in use, which yield an uninterrupted stream of air. Another primitive contrivance, known as the water-blast, is described in connection with the Catalan forge for smelting iron ores (Fig. 33). Blowing cylinders for producing a stream of compressed air are now generally used for smelting furnaces, such as are described for supplying the air to iron blast-furnaces. In the simple melting of metals, such as pig iron, in a cupola, a rotatory fan or blower is used. Root's blower is largely used for this purpose.

Hot Air.—If the air supplied to a furnace be previously heated, the temperature of combustion may be greatly increased, and as the waste heat of a furnace may be utilised in heating the air, a great economy is effected by its use. The

regenerative principle of heating was introduced by Siemens, and is now largely used in connection with open-hearth furnaces.* The regenerators are chambers of open refractory brickwork, containing a series of passages through which the waste gases from the furnace pass in their journey to the chimney, and thus give up their heat to the brickwork. When one pair of chambers has been sufficiently heated, the furnace gases are diverted to other pairs of chambers, and the previously heated pair are now used for heating gas and air respectively, which traverse them in inverse order, and thus pass over regions of gradually increasing temperature and enter the furnace at the maximum temperature, and by their union produce the maximum heat. In order that the spent gases shall not pass into the chimney at a higher temperature than 150° C., it is necessary to provide about 7 square feet of brickwork for every pound of coal burnt between the two reversals of the currents. (See also p. 148.) Air is also heated by conduction. This is well exemplified by the heating of the blast in iron smelting by means of cast-iron pipes heated externally, the air being forced through the inside and abstracts heat from the walls of the pipe. The same principle is employed in the Ponsard, Bœtius, and Bicheroux furnaces (Figs. 71, 72).

* See Figs, 82A, 82B.

CHAPTER VII.

FUEL.

BY this term is meant substances that may be burned in air to give heat capable of being applied to economic purposes. The two chief elements employed are carbon and hydrogen, the latter in fuels being always associated with carbon. In all fuels containing carbon, hydrogen, and oxygen, the proportion of hydrogen may be equal to, or greater than, but never less than that required to form water with the oxygen. The amount of hydrogen united with oxygen is not available as a source of heat, so that the excess of hydrogen over this amount is called " disposable" hydrogen, and the amount in combination the "non-disposable" hydrogen.

The amount of heat a unit weight of a body is capable of yielding when completely burnt is termed its *calorific power*. The heat is measured either by the number of the units of weight of water raised 1° C., or by the number of units of weight of water evaporated. The latter was proposed by Rankine, and gives numerical results 537 times less than the former. Except in this country, the gram-centigrade unit, termed a calorie, is generally used. This is the heat required to raise 1 gramme of water from 0° to 1° C. The British unit is the amount of heat required to raise 1 lb. of water 1° C. The following table is arranged in accordance with this unit :

Wood charcoal, ...	8080
Gas carbon, ...	8047·3
Artificial graphite, ...	7762·3
Native graphite, ...	7796·6
Diamond, ...	7770·1
Carbonic oxide, ...	2403
Carbon when burnt so as to form carbonic oxide, ... }	2473

Marsh gas (CH$_4$),	.	.	.	.	13063
Olefiant gas (C$_2$H$_4$),	.	.	.	.	11857
Native sulphur, .	.	.	.	.	2249
Amorphous silicon,	.	.	.	.	7830
Crystallised silicon,	.	.	.	.	7540
Phosphorus,	.	.	.	.	5747
Hydrogen, .	.	.	.	.	34462

The number 8080 for wood charcoal signifies that 1 lb. of that body when completely oxidised to carbon dioxide will produce sufficient heat to raise 8080 lbs. of water 1° C. ; and so on for the rest. The lower calorific powers of the denser forms of carbon are probably due to the absorption of heat in the mechanical work of breaking up the molecular constitution before the atoms are capable of uniting with oxygen. It will be observed that the densest form of carbon (diamond) yields the lowest calorific power. The calorific power of a fuel containing carbon, hydrogen, and oxygen, would be the sum of the calorific powers of the carbon and that of the disposable hydrogen.

The calorific power of a compound of carbon and hydrogen such as C$_2$H$_4$ may be calculated thus :—

$$\left.\begin{array}{l} C_2 = 24 \\ H_4 = 4 \end{array}\right\} \text{The atomic weight of carbon being 12 and that of hydrogen 1.}$$

$$\underline{28}$$

Then if 1 lb. be taken, $\frac{6}{7}$ will be carbon and $\frac{1}{7}$ will be hydrogen.

$$\frac{6}{7} \text{ of } 8080 = 6925\cdot7$$
$$\frac{1}{7} \text{ of } 34462 = 4923\cdot1$$

$$\overline{11848\cdot8}$$

Many hydrocarbons yield a less calorific power by experiment than by calculation, probably owing to the heat absorbed in their decomposition. Experiment and calculation only perfectly agree when the two elements are mechanically mixed, and not when they are chemically combined.

The instrument used for determining the calorific power of a body is termed a calorimeter. It consists essentially of a vessel in which the fuel may be so burnt that the heat produced may be imparted to a given weight of water, the increase in temperature of which serves to indicate the calorific power.
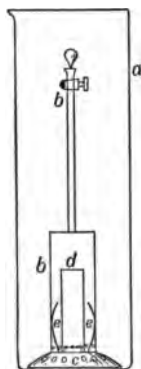
To determine the calorific power of a given fuel, carefully dry a quantity of finely powdered potassium chlorate and nitrate in separate dishes. Also a quantity of the fuel very finely powdered should be carefully dried. Weigh out 30 grains of the dried coal, 225 grains of potassium chlorate, and 75 grains of nitre; well mix and introduce into the perfectly dry copper tube of what is known as Thompson's or Wright's calorimeter; ram it moderately tight; insert a small piece of "fuse" (prepared by soaking cotton wick in a solution of nitre and drying it), and place the tube in the stand ready for the experiment. Now take the temperature of the water in the large vessel; light the fuse; cover with the bell tube, taking care that the tap is closed, and put the whole in the water before the ignited fuse has had time to burn down to the mixture. When the combustion appears complete, open the tap so that the water may absorb the residual heat in the tube, and again take the temperature of the water. The increase of temperature, plus 10 per cent. added for loss, gives the evaporative power of the fuel.

Fig. 19.

EXAMPLE:

Temp. of water before the experiment = 55° Fahr.
„   „   after   „   „   = 66°   „

„   produced by the combustion,   = 11
                    Plus 10%   = 1·1
                                     ———
Total evaporative effect,   =   12·1
                                     ════

i.e. 1 lb. of the coal on perfect combustion will generate 12·1 lbs. of steam.

(*a*) The apparatus (Fig. 19) consists of a tall glass cylindrical vessel *a* capable of holding 60,000 grains of water. At a given distance a mark is scratched on the outside to indicate 29,010 grains of water, which equals 967 × 30 (the former figure being the latent heat of steam and the latter the weight of fuel taken). A copper vessel (*b b*) fitted at the top with a stop cock; a perforated stand *c*, into the

socket of which the copper crucible d fits. This stand has three springs e for keeping the cylinder b tightly fixed to the stand. See also Fig. 11, p. 45.

Calorific Intensity.—This is the pyrometric degree of heat obtained when a body is completely burnt, and is theoretically the actual temperature of the products of combustion. It is based on the assumption that the products of combustion have constant specific heats for all temperatures and that they absorb all the heat produced, which is not the case. Heat is lost by conduction, radiation, and imperfect combustion, and dissociation also limits the temperature.

Suppose 12 grains of carbon to unite with 32 grains of oxygen to form 44 grains of carbon dioxide, or 1 grain of carbon to unite with 2·6 grains of oxygen to form 3·6 grains of carbonic acid, thus—

$$C + O_2 = CO_2,$$
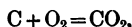
and the whole heat produced absorbed by this CO_2; that the pressure is constant and the specific heat of $CO_2 = ·2164$;

then the calorific intensity $= \dfrac{8080 \times 1}{3\cdot6 \times ·2164} = 10174.$

Now suppose the carbon burnt in ordinary air instead of oxygen. In this case nitrogen has to be heated without yielding anything to the calorific power. 1 part of oxygen in air is mixed with 3·35 parts of nitrogen, so that the weight of nitrogen to be heated when 1 part of carbon is converted to carbon dioxide is $2\cdot6 \times 3\cdot35 = 8\cdot93$. The specific heat of nitrogen is ·244.

Calorific intensity $= \dfrac{8080 \times 1}{(3\cdot6 \times ·2164) + 8\cdot93 \times ·244} = 2718° \text{ C.}$

The calorific intensity of carbonic oxide (CO) when burned in oxygen according to the equation,

$$CO + O = CO_2,$$
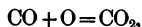
is 7073. One part of CO forms 1·57 parts of CO_2, then the calorific intensity $= \dfrac{2403}{1\cdot57 \times ·2164} = 7073,$

and in air $= \dfrac{2403}{(1\cdot57 \times ·2164) + (1\cdot91 \times ·244)} = 2984.$

The calorific intensity of hydrogen when burnt in oxygen is computed on the assumption that the water produced is

in the form of gas, therefore the condensation of that gas
to a liquid will absorb 537 units of heat. Also in raising
the water from 0° to 100° and from 100° to the temperature
obtained, we have first water with a specific heat of 1, and
afterwards steam with a specific heat of ·48, and $(1 - ·48) \times$
$100 = 52$; and as 1 lb. of hydrogen produces 9 lbs. of water
the above amounts have to be multiplied by 9, thus
$(52 + 537) \times 9 = 5300$. The calorific power of hydrogen is
therefore

$$\frac{(34462 - 5300)}{9 \times ·48} = 6750.$$

When the hydrogen is burnt in air the calculation is thus :—

$$\frac{34462 - 5300}{(9 \times ·48) + (26·8 \times ·244)} = 2685.$$

26·8 is the amount of nitrogen in the quantity of air required
to yield the requisite oxygen (8 parts) for 1 part by weight
of hydrogen.

Pyrometry.—By this term is meant the measurement of
high temperatures, and the instrument employed for this
purpose is termed a pyrometer. Pyrometers have been
constructed on the following principles :—

    1. By contraction in the volume of a body.
    2. By change of volume in gases, liquids, and solids.
    3. By dissociation of chemical compounds.
    4. By simple fusion of metals, alloys, etc.
    5. By conduction of heat by metals.
    6. By radiation.
    7. By thermo-electric methods.
    8. By electric resistance.
    9. By optical methods.
   10. By calorimeter methods.

    1. *Wedgwood's pyrometer* is based on the shrinkage of
dehydrated clay. Spherical pieces with one side flat and of
equal size are employed. He assumed that the shrinkage
was proportional to the temperature, but this is not strictly
so, and the method is only of advantage where relative
temperatures are required to be roughly measured.

    2. *Gauntlett's pyrometer* is based on the principle of the
different rates of expansion of different substances. A
metallic rod is placed in a hollow cylinder of refractory
material, and the difference of expansion is registered by
causing the bar in expanding to move an index of infusible
material within the cylinder.

Deville and Troost applied the principle of the air thermometer to the measurement of high temperatures. Into a flask of porcelain of 300 c.c. capacity, having a long neck, is placed a little iodine. It is then inserted in the hot space until the iodine is vaporised and the air nearly expelled. The neck is then sealed with a blowpipe and the flask cleaned and weighed when cool. The neck is then broken under water, and the flask with the water which has entered again weighed; it is then completely filled with water and again weighed; and finally the flask is weighed when empty. From these weighings the amount of residual air which was not expelled by the iodine is computed, as well as the

L. Lamp.
M. Mirror.
G. Galvanometer.
R. Reflector.
S. Screen.
W. Thermo-junction.
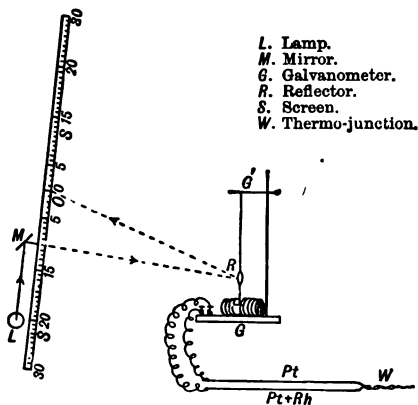
Fig. 20.

capacity of the flask; and the amount of iodine at the time of sealing. Now knowing this amount of iodine and the volume it occupied at the same moment the temperature may be computed according to Boyle's law.*

4. *The principle of the simple fusion of bodies* of known melting points, such as the common metals and certain alloys, is the simplest method of measuring temperatures where only approximate results are needed. This method is used for determining the temperature of the hot blast.

5. *Conduction of heat* has been applied to the measurement of the temperature of a furnace by inserting in it one

* *Watt's Dictionary,* Vol. III., p. 20.

end of an iron bar, and at the other end of the bar is a hole in which a mercurial thermometer is placed. This method is only approximately correct. Carnelly and Burton described a new form of pyrometer on this principle to the Chemical Society, 1884. "If a current of water of known temperature be allowed to flow at a constant rate through a coiled metallic tube, placed in a space, the temperature of which is to be ascertained, the increase in the temperature of the outflowing water will be the greater the higher the temperature of the space."

7. *Thermo-electrics.*—This appears to be the most reliable pyrometric method yet devised, and of thermo-couples the one introduced by Le Chatelier is the best. A diagrammatic view is shown in Fig. 20. It consists of a wire of platinum and a wire of an alloy of platinum with 10 per cent. of rhodium either twisted or soldered together. When this thermo-electric junction is heated a current of electricity is generated, and the current is sent through the coils of a reflecting galvanometer, the amount of the deflection of the mirror connected with the magnetic needle being proportional to the heat applied to the junction. The instrument is calibrated by taking certain well-known temperatures, such as the melting point of silver, boiling points of zinc, sulphur, etc. For fuller information the reader should consult Roberts-Austen's work on Metallurgy and *Journal of Iron and Steel Institute*, 1892-1894.
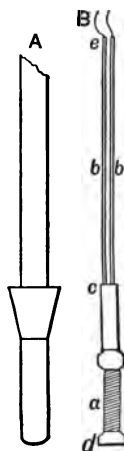
8. *Electric Resistance Method.* — Siemens' electric resistance pyrometer is represented in part in Fig. 21. It consists of a platinum spiral (*a*) of known resistance, wound on a cylinder of fire-clay, and enclosed in a casing of platinum or copper, according to the temperature to be measured. The two ends of the coil are connected by thick platinum wires with two thick copper wires, at the part which is less strongly heated. These wires are insulated by pipe-clay tubes (*bb*) and communicate with the measuring instrument by which the resistance is measured. The electric resistance of platinum is increased fourfold by a rise in temperature from 0° to 1650° C. The portion (*cd*) which is exposed to the highest temperature of the furnace is encased in wrought

Fig. 21.

iron or platinum, and the outer portion (*ce*) is enclosed in an iron tube. The outer tube is shown in Fig. 21 A, and the resistance arrangement in Fig. 21 B.

9. *Optical Method.*—The pyrometer of Mesuré and Nouel depends on the partial rotation of polarised light by a quartz plate ; the rotation varies with the intensity of the light, and by measuring this the temperature of the substance which emits the light can be determined. A quartz plate is placed between the polarising and analysing prisms, the latter being turned until a definite neutral tint between green and red is
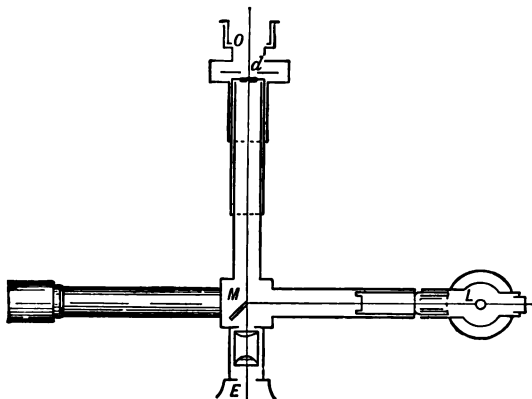
Fig. 22.

produced. The angle is measured by reference to a prepared table.*

The Cornu—Le Chatelier pyrometer consists of a telescope associated with a standard of comparison oil lamp. The flame is projected upon a mirror fixed at an angle of 45° and placed internally across the junction of the lamp tube branch with that for sighting the incandescent object. The intensity of the luminous beams from the lamp and that from the fur-nace, whose temperature is to be measured, is equalised, and the degree of adjustment required enables the temperature to be determined. Fig. 22 shows a plan of the pyrometer ; *L* is the lamp the beams from which are projected on to

* *Introduction to Metallurgy*, Roberts-Austen, p. 159.

the mirror M by means of a lens and reflected along the branch containing the eye-piece E. The object glass O has a diaphragm or stop d in front. In cases of a very dazzling light a tinted glass may be fixed in the mounting E. Before the eye-piece there is fixed a monochromatic red tinted glass which serves for the purpose of observation of the object to be tested. Near the oil lamp there is fixed a rectangular set of stops similar to those before the lens O. They serve for fixing the height of the oil flame and for intercepting the extraneous rays. In order to measure the intensity of the heat of the incandescent body, the height of the flame should remain constant, and the luminous beam from the lamp should be divided into two equal parts by the edge of the mirror M. This can be obtained by turning the lamp on its mounting.

In order to take a measurement the object glass is turned towards the furnace, or other incandescent surface to be tested, in such a way that its image is cut in equal divisions by the edge of the mirror, and is thus brought into contact with the image projected from the light of the oil lamp. The opening of the shutter diaphragm aperture, and the variation of the intensity of the beam projected from the incandescent surface, is effected by turning the screw knob on the object telescope, so that by this means the equality of intensity of the two images is established.

If n is the number of divisions read upon the graduated scale fixed on the tube of the object glass, and indicating the degree of adjustment of the shutter diaphragm of the lens O, and n' is the number of divisions obtained on sighting the source of light from the standard lamp, the intensity of heat sought for will be obtained by the formula—

$$\left(\frac{n'}{n}\right)^2 = 1 \text{ (intensity of heat)}.$$

In other words the intensity is equal to the inverse ratio of the superficies of the opening of the shutter diaphragm fronting the lens O.

10. *Calorimeter Method.*—Pouillet exposes a ball of copper or of platinum of given weight to the heat of the furnace, and then rapidly transfers it through a clay tube to a vessel containing a known weight of water, at a known temperature. From the increase in temperature of the water the temperature of the furnace is calculated. The mode of calculation is as follows:

$$T = \frac{W \times (t' - t)}{w \times s};$$

T is the temperature, $t' - t$ the rise in temperature of water, W the weight of water, w the weight of ball, and s its specific heat. To this result must be added the observed temperature of the water.

Wood is composed of organic tissue, termed cellulose, and a little other organic matter as sap. Cellulose may be regarded as a compound of carbon and water, since the proportion of oxygen to hydrogen is as 8 : 1, and practically only the carbon is available as a source of heat. Its formula is $C_6H_{10}O_5$, and it contains 44·44 per cent. of carbon, 49·39 per cent. of oxygen, and 6·17 per cent. of hydrogen. A small proportion of inorganic matter is also present, and forms the ash when the wood is burned. It consists of 70 per cent. calcium carbonate, 20 per cent. alkaline carbonates, and varying amounts of chlorides, sulphates, phosphates, and silicates. Wood always absorbs hydroscopic water, which may be removed by heating it at a temperature of 120° C. The moisture is also partially removed by air-drying, but even then it retains 20 per cent. of moisture. This greatly limits its calorific power.

Peat (or Turf) is the product of the decomposition of various vegetable substances, chiefly mosses, under the combined influence of air and moisture, which induce slow decay. The deeper the peat the darker and denser it is, and the less the remains of vegetable structure. The composition varies with the proportion of water and inorganic matter which it has contracted from the earth, the ash sometimes reaching 30 per cent., and is rarely below 10 per cent. This ash consists of silicates of calcium and iron, together with some phosphates, carbonates, and sulphates, also a little alkali, alumina, and magnesia. Peat is dried and often compressed before being used, and even then it may retain 25 per cent. of moisture. The colour varies from light brown to black.

Lignite.—This fuel forms a connecting link between peat and coal, and may be divided into : fossil wood, earthy lignite, dry lignite, and bituminous lignite. It is the same as the brown coal of the Germans. Lignite burns with a long smoky flame, and contains considerable moisture, which limits its calorific power. Bituminous lignite is used for the production of tar, and the other varieties as fuel. The proportion of ash varies as in peat, and consists of lime, silica, alumina, magnesia, with some alkalies and oxide of iron, but no phosphoric acid.

Coal is of vegetable origin, and resembles wood and peat

in character the more modern the formation in which it is found. It may be divided into two distinct classes—Coal and Anthracite—the first being the least altered and the last the most completely changed. As we descend the series, the oxygen diminishes and the carbon increases ; but the chief characteristic of different kinds is the ratio of hydrogen to oxygen, and the carbon left on distillation in a closed vessel. In lignites the ratio $\frac{O}{H}$ varies from 6 to 5, and the coke is below 50 per cent. In coal the ratio $\frac{O}{H}$ varies from 4 to 1, and the coke from 50 to 90. In anthracite the ratio $\frac{O}{H}$ is 1 or less than 1, and the coke exceeds 90 per cent.

Coal is distinguished from lignite by a more pronounced black colour, greater density, more friability, more laminar structure, absence of woody fibre, a greater yield of coke, less water in the products from distillation, and that rather basic than acid, and the absence of the disagreeable odour of lignite when burning. In the natural state coal contains but little water, and is less hygroscopic in air than wood or lignite.

Coal, by its appearance, properties, and composition, forms a continuous series from lignite to anthracite, with no definite line of separation. The proportionate yield of coke is from 50 to 90 per cent., and the elementary composition as follows :

Carbon,	.	.	.	.	75 to	93
Hydrogen,	.	.	.	.	6 to	4
Oxygen,	.	.	.	.	19 to	3
					100	100

The first column belongs to coal bordering on lignite, the second column to that approaching anthracite. Between these extremes are varieties with intermediate properties.

Coal may be conveniently divided into five classes, based on the yield of coke and action in the fire : 1. Long flaming coal ; 2. gas coal ; 3. forge coal ; 4. caking coal ; 5. lean or anthracite coal.

Long Flaming Coals, approximate in properties to lignite on the one hand and to caking coals on the other. They are non-caking, give a long smoky flame when burning. They occur abundantly in Scotland, also in Derbyshire and Staffordshire. The calorific power is 8000 and upwards.

Gas Coals are only moderately caking, some varieties yielding a very friable coke. These give off much volatile matter when heated, and yield a long smoky flame. The calorific power is about 8500, and they give off about 20 per cent. of gases.

Forge Coals.—These are moderately hard and dense, with a black colour and fatty lustre. The calorific power is about 9000. They burn with a fairly long smoky flame, and generally yield a good compact coke, and evolve 15 to 16 per cent. of gases.

Caking Coals with Short Flame.—These are the best caking coals, and yield a hard, dense, compact coke, and liberate 12 to 15 per cent. of gases. The calorific power is about 9500.

Anthracitic Coals.—These burn with a short flame, and form a connecting link between caking coals and anthracite proper. The calorific power is about 9300. They occur abundantly in South Wales and in Pennsylvania.

Anthracite is compact, of a deep black colour and a lustre bordering on the metallic ; it is brittle, breaks with an uneven or conchoidal fracture, has a high degree of hardness and cohesion ; it inflames and burns with difficulty, giving an almost smokeless flame. Some varieties easily decrepitate. It yields neither water nor bitumen in sensible quantities when heated, and the fragments neither fuse nor change their lustre nor cake together. It may be looked upon as the most completely changed form of vegetable matter in its conversion into coal.

Petroleum.—In various parts of the earth are found combustible bodies similar to "petroleum," which contain a large amount of ash. They are solid, liquid, and gaseous hydrocarbons, rich in carbon. Marsh gas and olefiant gas are gaseous. Petroleum proper is liquid. The asphalte of Mexico is a kind of solid petroleum which fuses below 100° C. An analogous compound to asphalte is "boghead" of Scotland, and is richer in bitumen than ordinary coal. When the earthy matter diminishes to the proportion present in ordinary coal, it takes the name of "cannel" coal. The natural mineral called jet occupies an intermediate place between coal and petroleum. It is a bituminous lignite, and disengages, when heated, 55 to 60 per cent. of volatile matter containing 5 to 6 per cent. hydrogen.

Natural Gas.—In certain parts of the United States, chiefly in Pennsylvania, West Virginia, and Ohio, natural gas issues from the earth, proceeding from strata 800 to 2000

COMPOSITION OF VARIOUS FUELS AFTER COMPLETE DRYING (GRUNER).

Name	Percentage of composition			Proportion of oxygen per 1000 of carbon.	Proportion of hydrogen per 1000 of carbon.	Ratio of $\frac{O}{H}$	Charcoal or coke obtained by heating the dry material in form of powder.	Nature of the charcoal or coke obtained.	Calorific power.
	Carbon.	Hydrogen.	Oxygen.						
Cellulose, .	44·44	6·17	49·39	1111	139	8	28-30	Pulverulent.	...
Wood, .	50-51·75	6-6·30	44-41·95	8 0-800	120-122	7	30-35	Do.	...
Peat, fossil wood, .	58-63	6-5·5	36-31·5	620-500	100-85	6-5	35-40	Do.	3000 to 5000
Lignites, .	65-75	6-4	29-21	450-280	92-55	5	40-50	Do.	5000 to 7000
Coal, poor, with long flame, .	75-80	5·5-4·5	19·5-15	200-190	75-60	4-3	50-60	Pulverulent, slightly fritted.	
Coal, rich, with long flame, .	80-84	5·8-5	14·2-10	180-120	70-60	3-2	60-68	Caked, very tender.	8000
Coal, ordinary, rich, .	85-89	5-5·5	10-5·5	130-60	65-56	2-1	68-74	Caked, moderately compact.	8500
Coal, rich, with short flame, .	88-91	5·5-4·5	6·5-4·5	70-50	62-50	1	74-82	Caked, very compact.	9000
Coal, anthracitic, .	90-93	4·5-4	5·5-3	50-40	50-35	1	82-90	Fritted or Pulverulent.	9500
Anthracite, .	93-95	4-2	3-3	40-25	35-30	1-0·75	90-92	Pulverulent.	9300
Petroleum, .	80-85	15-14	3-1	30-15	185-175	0·20-0·10	...	...	...

feet below the surface, and when bore-holes are sunk, the gas rises at a pressure of 150lbs. per square inch. This gas is used for illuminating and heating purposes. The composition varies within the following limits: 60 to 80 CH_4, 5 to 20 H, 1 to 12 N, 1 to 8 C_2H_6, ·2 C_2H_4, and ·3 to 2 CO_2. It has a calorific power of 14,000 to 15,000. One gas well alone in Ohio has been blowing for twenty years without any apparent diminution.

PREPARED FUEL.

Certain fuels, as soft peat, coal dust, etc., are unsuitable for use in the natural state, but may be prepared by compression, as in peat; or caked, as in coal dust, by mixing it with coal tar, pitch, or other cementing material. Wood and peat have their calorific powers increased by artificial drying.

Wood Charcoal.—When wood is heated to a temperature of 400° out of contact with air; water, acetic acid, tar, carbon dioxide, carbonic oxide, hydrogen, marsh gas, etc., are given off, and a black, sonorous, hard mass of charcoal is left. At a lower temperature—270° to 300° C. it is more or less brown, feebly sonorous, but more tenacious than black charcoal. Charcoal always retains some oxygen and hydrogen, but the amount is less the higher the temperature employed in its production. On an average it contains 90 per cent. carbon, 3 per cent. hydrogen, and 7 per cent. oxygen. The specific gravity varies from ·28 to ·54, according to the nature of the wood and the temperature employed. The ash left on combustion is 3 to 4 per cent., and of the same character as that of wood.

Peat Charcoal.—The shape of the peat is preserved like that of wood when heated in closed vessels. It is black in colour, porous, soft when prepared from peat in its native state, and more compact and dense when prepared from compressed peat. It, like wood and charcoal, retains some volatile elements.

When steam is passed over red-hot charcoal,—hydrogen, carbonic oxide, carbon dioxide, and a little marsh gas are formed.

Making Charcoal in Piles.—The ground should be dry, well sheltered, and near a water supply. The bed is slightly inclined from the circumference to the centre. One or three stakes, long enough to reach above the upper extremity of the intended mound are first driven in the ground

in the centre of the circle. Around this the wood, cut into suitable lengths, is packed as closely as possible, being placed in a vertical or horizontal direction, and all irregular spaces filled up with small twigs. The wood is then encircled and covered with branches, and the upper portion is covered with turf and charcoal dust, leaving a certain part open at the base for the escape of aqueous vapour during the first stage. The space between the three stakes is filled with readily-inflammable wood, which is ignited to start the operation. The wood in the central part of the pile is charred first, then covered up, the combustion proceeding from top to bottom and from the centre to the outside of the heap. Vents are made at suitable intervals, commencing at first near the top, and closed when the carbonisation in that
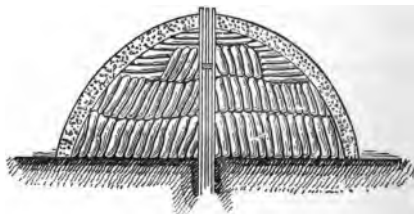
Fig. 23.

region is complete, which is judged by the pale blue colour of the smoke (Fig. 23).

2. In some cases rectangular piles are used ; in others the charring is effected in kilns and in ovens. The heat by which the carbonisation of wood is effected in piles is produced by the combustion of charcoal itself, and not by the burning of the products of carbonisation. The yield varies with the nature of the wood, its age, dryness, and the temperature and mode of charring. By volume the yield varies from 50 to 75, and by weight from 15 to 28 per cent. Peat may be carbonised in much the same way as wood—in piles, in kilns, and in ovens—but it is not suitable for most metallurgical purposes.

COKE.

Coke is obtained when coal is strongly heated, in a closed space or vessel, with a limited supply of air. It may be

porous and light, or dense and compact ; it is sometimes soft
and tender ; at others, hard and resisting. The colour varies
from black to grey, the lustre being in some cases dull, in
others bright and almost metallic. The quality depends on
the nature of the coal and mode of coking. Nearly all coals
contain iron pyrites (FeS_2), and a part of the sulphur remains
in the coke. The coke from caking coal has the appearance
of a porous, partially melted mass, which is grey in colour,
with a semi-metallic lustre. The coke from flaming coal is
lighter and more friable. The rapid carbonising of a small
charge gives a lighter and more friable coke than the slow
baking of a heavy charge. Dry coke with little ash is lighter
than water. It is hygroscopic like charcoal, but in a less
degree. Coke is less inflammable and less combustible than
charcoal, but produces a higher temperature on burning.

Coking in Piles.—Coking is effected in circular and rect-
angular piles, like charcoal. A rough chimney of loose bricks
is first constructed, 6 feet high, capped with a damper, and
the coal arranged around it, making a mound 30 feet in
diameter at the base. The whole is then covered with wet
slack, except a space around the bottom. Ignition is effected
by placing live coals on one side of chimney, near the top,
and continued by opening vents in different parts, as in
charcoal burning. The coking is completed in about six
days.

Coking in Kilns.—Two parallel walls (AA, Fig. 24),
5 feet high and 8 feet apart, lined with fire-brick, are first
built with a series of open-
ings (BB), 2 feet apart, and
the same distance from the
floor, so arranged that those
on one side are opposite to
those in the other wall ;
and from each of these
ascends a vertical flue (cc).
Any of these flues may be
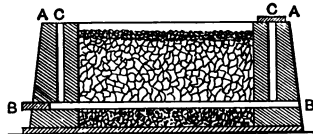
Fig. 24.

stopped by closing with a tile, so as to divert the current
in any given direction. To charge the kiln, one end is bricked
up, wet slack is wheeled in, spread in layers and stamped
down, reaching nearly to the level of BB. Wood stakes are
now placed across, the ends reaching into the corresponding
opening in the opposite wall. The coal is then wheeled in,
watered, stamped down, the other end bricked up, and the
whole covered with loam. The stakes are now withdrawn,
and the kiln lighted by inserting inflammable sticks. The

charring is completed in about eight days. The whole is allowed two days to cool, and the coke is then withdrawn.

Coking in piles and kilns does not produce a uniformly coked product, and much of the coke is itself consumed so that these methods are wasteful, and have been largely superseded by the use of ovens of various shapes and methods of working, the aim of which is to produce the requisite heat by the combustion of the waste gases without burning the coke itself.

The Beehive Oven (Fig. 25) is a somewhat circular chamber of brickwork with an arched roof, having a chimney opening at the top for the escape of the products of combustion and vapours, and for charging. The internal capacity is about 9 feet to 10 feet in diameter, and 3 feet to 4 feet high. The charge is sometimes introduced through a doorway in front, about $2\frac{1}{2}$ feet square, through which the charge is also withdrawn. These ovens are generally built in two rows back to back, with a charge of three tons in each, which reaches up to the springing of the dome of the roof. When the charging is complete, the doorway is loosely filled up with bricks, through the openings of which the air can pass. Supposing the oven to be hot from a previous charge, in three hours the lower holes are closed, and in twenty-four hours the upper ones are closed. The oven is now allowed to remain twelve hours with the chimney open. When the flame ceases, the damper is closed, and the oven allowed forty-eight hours to cool. The charge is then withdrawn by means of a large shovel suspended by a crane, and the hot coke quenched with water. There is a partial combustion inside the oven, so that some of the coke is burnt.
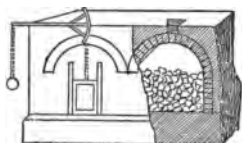
Fig. 25.

Cox's Oven is a nearly rectangular fire-brick chamber of the beehive type, closed with an iron door lined with fire-brick. The coking space has a double arched roof, forming a space through which the gaseous products pass before reaching the chimney, so as to utilise some of the waste heat. At each side of the door is an opening leading by a flue to openings in the back of the chamber, for the introduction of air heated by passing through this flue, thus raising the temperature of the oven. The coking chamber is slightly wider in front, and the floor also slopes from back to front, which facilitates withdrawal of the charge.

Jameson's Coke Oven is represented in Fig. 25A, converted from the ordinary beehive form, for the recovery of volatile products. The difference between a Jameson oven and one of the usual type consists in the use of a false bottom over a closed bottom below it, and in the removal by aspiration, from between those bottoms, of the gases given off from the coal as the heat travels from the top downwards. Mr. Jameson lays stress upon the fact that in coking coal, by the agglomeration of particles, a species of crust or sealed diaphragm is formed in the charge of coal, which acts as a shield, against the passage of air or burnt gases from the upper part of the oven, towards the reduced pressure in the lower part, and at the same time imprisons the gases formed below it,
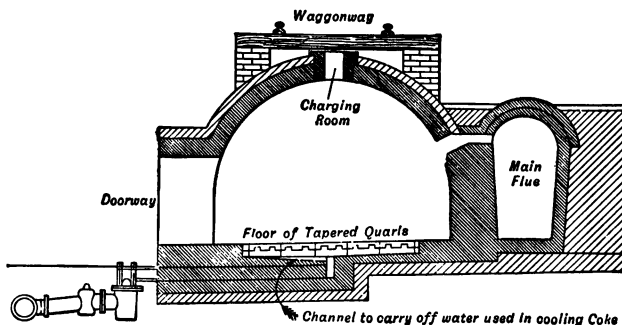
Fig. 25A.

so as to facilitate their removal by the aspirator. Another point to which he attaches great importance is, that in the progress of coking the suction applied to the oven itself should be varied within somewhat wide limits; that is to say, that when the gas is forming near the top of the oven, and is to be drawn through a mass of unheated coal 2 feet or 3 feet thick, there should be a suction equivalent to 2 or 3 inches of water pressure to overcome this resistance, and when the charge in the oven is nearly coked throughout and the gas is formed near the oven bottom, then the suction should be diminished to a pressure perhaps of half an inch of water. The suction, he also points out, should be fixed in reference to the chimney draught, which is, of course, a counteracting influence operating with different force as the

oven is more or less closed to the external air. The varia-
tion of suction he proposes to make once a day, or at most
once in twelve hours, by means of a regulator. Another
point of importance is the construction of the oven bottom.
The true bottom should be as well secured as possible
against ingress of air, and the false bottom should be so
constructed as not to allow passage for small coal, and yet
sufficiently open so as not to become choked up with
hardened deposits arising from the carbonising of the tar
and coal dust.

In the more recent forms of coke oven air is not admitted
into the coking chamber, but into side flues, so as to burn
the gases outside the oven and thus prevent loss of coke.
Moreover, the waste gases are completely burnt, and the
heat utilised in heating the oven instead of allowing them to
escape, as in the beehive oven. Of this type the Appolt,
Coppée, and Carvé may be mentioned.

Appolt's Oven.—Eighteen vertical retorts of brickwork
are built in two rows of nine each, the whole being contained

Fig. 26.

within four brickwork walls. Each
retort is rectangular in plan, sur-
rounded by an air space 8 to 10 inches
wide. The retorts (Fig. 26) are tapered,
measuring 1 foot 1 inch by 3 feet 8
inches at top, and 1 foot 6 inches by 4
feet at base, and 16 feet high. Each
retort is provided with a cast-iron
door at the bottom, opening into an
arched vault, into which the coke is
dropped at the conclusion by opening
this door. The air spaces surrounding
each retort communicate with one
another, forming one large divided
chamber, which communicates with the
inside of the retorts by openings in
the brickwork. It is in this divided
chamber that combustion of the pro-
ducts of decomposition of the coal takes place, air being
admitted through holes in the outer sides of the kiln.
By this arrangement a very great heating surface in propor-
portion to the capacity of the oven is obtained, with a very
high efficiency in coke produced. The oven is charged with
coal at the top, and the time of one operation, starting with
hot retorts, is about twenty-four hours. The charge is 1 ton
5 cwt. for each chamber. The great drawback seems to be
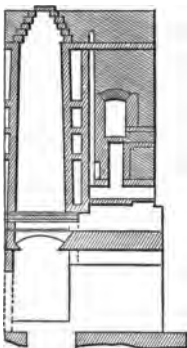
the high initial cost, which is double that of a horizontal oven, and it is also difficult to repair when out of order.

Coppée's Oven (Fig. 27).—This is constructed like the Appolt oven, for heating by the combustion of the waste gases in external flues, but the axis of this oven is horizontal. It is only used for finely divided coal, its chief advantages being rapid coking and an increased yield. Some coals that are not sufficiently bituminous for coking in an ordinary oven may be coked in the Coppée oven. They are usually built in a series of 30 or 40 and worked in pairs. Each oven is 30 feet long, 18 inches wide, and 4 feet high, and contains twenty-eight vertical flues leading from the top,
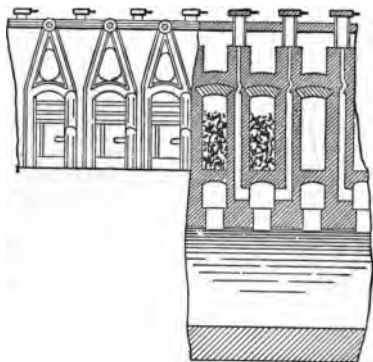
Fig. 27.

through the partition wall common to two ovens, to the horizontal flues that pass underneath the chamber in the direction of their length. In these horizontal flues, the gases from a new charge of coal mix with those from another oven in which the coking is nearly completed, and air is admitted through three small openings. After combustion, the flame passes to a bottom flue, giving up a portion of its heat to the bottom of the oven. When the coking is complete, the charge is pushed out by a ram and quenched with water.

Carvé's Oven.—This excellent oven (Fig. 28) has the reputation of producing high-class coke, and of being also well adapted for the recovery of the by-products—tar and ammoniacal liquors. Each oven is a long, narrow, and high

brickwork chamber, A, resembling that of Coppée, with hori-
zontal flues penetrating the side walls, as shown in dotted
outline, BB. These flues communicate with two horizontal
flues, CC, running under the floor of each chamber. The pro-
ducts of combustion from the fireplace, E, pass through CC,
and then ascend to the uppermost of the side flues, BB.
From thence they traverse backwards and forwards along
the sides of the chamber, finally passing into the flue, D, and
thence into the chimney. The products of carbonisation are
drawn off by an exhauster through F and the valve G into
condensers, where the gases are freed from the ammoniacal
liquors and tarry oils with which they are associated. The
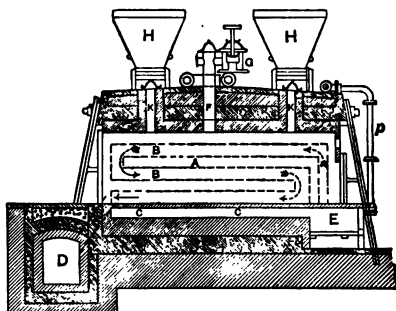
Fig. 28.

gases are then brought to the fireplace, E, by a pipe, *p*, and
ignite as they pass over the burning fuel. The resulting
flame then traverses the bottom and sides of the oven as
described above.

In a more recent oven the fireplace is dispensed with and
the oven heated entirely by the return gases, air for the
combustion being forced in through a special pipe. In the
Simon-Carvé oven the air is previously heated to 500° by
contact with the flues conveying away the spent gases to the
chimney. The air is not admitted into the bottom flue in
sufficient quantity for complete combustion of the gas, and a
further supply of hot air is admitted into the side flues for
complete combustion. Each oven is about 24 feet long,
6 feet 6 inches high, and 20 inches wide, and takes a charge
of about 4½ tons of coal.

The coal for coking is charged through the hoppers, HH.

When the charging is complete, the passages, KK, are closed, and the doors closing the ends of the ovens carefully luted to prevent admission of air. This prevents loss of coke by combustion at the surface of the charge, and 15 per cent. more coke is obtained than is produced in an ordinary bee-hive oven.

Composition of Gases.—The composition of the gases liberated from coke ovens during coking varies with the time and mode of coking. The mean of some experiments by Ebelmen gave 10·93 of carbonic acid, 3·42 of carbonic oxide, 1·17 of marsh gas, 3·68 of hydrogen, and 80·80 per cent. of nitrogen, the first and last being non-combustible. The waste gases of coke ovens have been utilised for heating the ovens themselves, heating boilers, and for the recovery of tar, ammonia, etc.

Desulphurisation of Coal.—Sulphur exists in coal in two ways—firstly, in greatest proportion in pyrites; secondly, in sulphate of lime. During coking half the sulphur is driven off from the pyrites, but the whole of that in the sulphate of lime is retained. It is therefore a disadvantage to have sulphate of lime in coal to be used for making blast furnace coke, but a great advantage if the coal has to be burned in an open grate or in a separate fireplace, since the sulphate is retained in the ash and none of it passes into the gases. Coal is often crushed and washed in order to remove pyrites. Sulphur then is removed partially from coal in two ways (1) by washing, (2) during the coking process.

Gaseous Fuel.—By the use of gaseous fuel it is possible to utilise common varieties of solid fuel and waste products for its production, and also to obtain higher temperatures than ordinarily prevail when burning solid fuel directly on a grate; gaseous fuel leaves no cinder or ash; a higher calorific power may be obtained on account of the smaller quantity of air required for combustion, and therefore less inert nitrogen is present to absorb heat. In burning coal or carbonaceous matter in a limited supply of air, or by causing air to pass through a thick layer of incandescent fuel, carbonic oxide is largely produced, because any carbon dioxide is decomposed by the highly heated carbon. The following is a typical composition of producer gas : 33 of carbonic oxide, CO ; 2 of carbon dioxide, CO_2 ; 2 of hydrogen, H ; $3\frac{1}{2}$ of marsh gas, CH_4, and $59\frac{1}{2}$ per cent. of nitrogen, N. If the temperature be allowed to rise too high through too much air being admitted, then more CO_2 will be produced and less of combustible gases.

Siemens' Gas Producer (Fig. 29) is a nearly rectangular chamber lined with fire-brick, 6 feet wide, 6 feet deep, and 3 feet from front to back. The side A is formed of iron plates lined with fire-bricks, having a step grate B and wrought iron bars C. The fuel is charged through the hopper D. The gas passes up the pipe E, which is cased with iron, and thence into a horizontal wrought-iron pipe, which conveys it to the regenerator. The combustible portion of the gas consists chiefly of carbonic oxide (CO) termed "air" gas. When a jet of steam is introduced the gas liberated also contains hydrogen.

Fig. 29.

The Wilson Gas Producer (Fig 30) is used in connection with two steam jets, and works under a slight pressure. Fine slack can be used. It is a closed circular iron vessel,
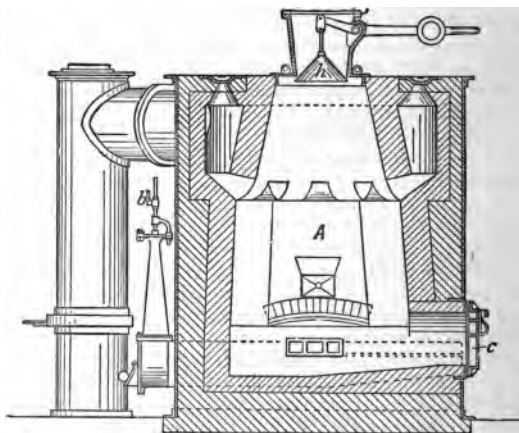
Fig. 30.

lined with fire-brick, and having a solid hearth, so that forced air is required. This is effected by means of steam jets directed into a conical trumpet-mouthed nozzle, and by

its injection drags air into the pipe. The blast enters the inside of the producer through a T-shaped distributor, and consists of 5 to 10 parts of steam to 100 parts of air. The producer is about 8 feet in diameter, and burns 4 cwt. of coal per hour.

Water-Gas.—When steam is passed over incandescent coke or carbon the water is decomposed and a mixture of carbonic oxide and hydrogen is produced; this is termed water-gas. A large cylinder of iron is lined with fire-brick, and at the top is a kind of cup and cone arrangement for charging the coke, which is the combustible used. Supposing the chamber to be hot from a previous operation, a forced blast of air is introduced until the whole mass is in an incandescent state. The blast is then stopped, the charging hole closed, and a current of steam is blown through the red-hot coke. The oxygen unites with the carbon, forming carbonic oxide, and the hydrogen is liberated. Water-gas therefore consists of equal volumes of carbonic oxide and hydrogen, as shown in the equation :—$H_2O + C = CO + H_2$, or a ratio of 14 : 1 by weight. Such a gas is very valuable for purposes where a very high local temperature is required. Now, as mentioned above, some of the carbon is first burnt by air and forms ordinary producer gas, and as air contains a large proportion of nitrogen, the product is a mixture of gases of which 60 per cent. is inert nitrogen. The producer gas thus obtained has burnt 75 per cent. of the carbon, so that only 25 per cent. of the total carbon is burnt to the condition of water-gas. If the whole of the carbon could be burnt direct by steam, then water-gas would be very economical : 75 parts of carbon will yield 551·19 parts of producer gas, of which 175 parts are carbonic oxide ; 25 parts of carbon will yield 62·5 parts of water-gas, of which 4·16 is hydrogen, and 58·34 is carbonic oxide. The amount of heat produced by the combustion of the above producer gas is nearly double that obtained by the combustion of the above water-gas. For ordinary heating purposes at very moderate temperatures the direct use of solid fuel is preferable to that of gaseous fuel, but where very high temperatures are required gaseous fuel is to be preferred, because with it the principle of regeneration can be applied, and a less volume of air is required for complete combustion, and therefore less heat is wasted in the chimney gases. The addition of steam to an ordinary gas producer, such as Wilson's, causes a richer gas to be produced, due to about 10 per cent. of free hydrogen, which gives such gas a higher calorific power.

H

Now water-gas with its comparatively high calorific power possesses only about half the heating power of coal gas, but it burns with a smokeless flame of such small size as to give a local temperature much higher than that of a coal-gas flame. Unfortunately water-gas is five or six times as poisonous as coal-gas. It is also scentless, so that some odorous gas has to be mixed with it to render its presence known. For fuller information see *Journal of Iron and Steel Institute*, Vol. II., 1889.

CHAPTER VIII.

IRON.

Ores of Iron.—Iron rarely occurs in the metallic state, which is probably due to its affinity for oxygen and other non-metals. Large masses of iron, known as meteorites, are occasionally found in different parts of the world; they are easily distinguished from terrestrial ores by containing nickel, and the metal is usually found in a mass containing crystals. The mass is nearly always covered on the surface with a thin coating of oxide, which protects the metal from oxidation. Iron occurs in a great variety of minerals, but the oxides and carbonates are almost the only forms utilised by the smelter.

Magnetite or Magnetic Iron Ore.—When pure it contains 72·41 per cent. of iron, and is represented by the formula Fe_3O_4. It is sometimes crystalline, but more generally massive. It is black or dark brown in colour, brittle, magnetic, and leaves a black streak when drawn across a plate of unglazed porcelain; it has a specific gravity of about 5·2. It occurs in granite, gneiss, clay-slate, hornblende, chlorite, and occasionally in limestone. Nearly all the Swedish iron is obtained from this class of ore, which also occurs in great abundance in the island of Elba, and in the United States of America.

Franklinite.—This ore is similar in colour to magnetite, but less magnetic, occurring in crystals and massive. It gives a dark reddish-brown streak, and has a specific gravity of about 5·1. It consists of ferrous and ferric oxides, manganous and manganic oxides and oxide of zinc. It is chiefly found in New Jersey, and is used as a source of zinc and spiegel-eisen.

Hæmatite.—Composition Fe_2O_3, containing 70 per cent. of iron when pure. It exists in crystals, in fibrous, colum-

nar, kidney-shaped, granular, and compact forms. Its colour varies from dark iron-grey in the crystallised, to deep red in the compact varieties. Its specific gravity is as high as 5·3 when in crystals, and as low as 4·2 in earthy varieties. Special names are given to different forms, thus :—Specular ore, as in the brilliant crystalline species of Elba and Brazil. Micaceous ore, as in the scaly varieties of South Devon. Kidney ore, as that from Cumberland. Red ochre is a compact earthy variety, often containing clay. Puddlers' ore is a compact, unctuous form from Cleveland, and used for lining puddling furnaces. Spanish or Bilbao ore is a siliceous hæmatite containing manganese, and noted for its purity, hence its use in the open-hearth steel process.

Ilmenite or Titaniferous Iron Ore.—This is a dead black mineral, generally found massive, consisting of ferrous and ferric oxides, titanic oxide and magnesia. It gives a brownish streak, and its specific gravity varies from 4·5 to 5. It may be typically represented by the formula $FeO . TiO_2 + MgO . TiO_2$.

Turgite.—This is an ore resembling hæmatite in colour and streak, but is hydrated, consisting of 94·7 per cent. of ferric oxide and 5·3 per cent. of water. Formula, $2Fe_2O_3, H_2O$.

Brown Hæmatite is a hydrated ferric oxide. It varies in colour from blackish to yellowish-brown, and gives a yellowish-brown streak. The following are the different varieties :—

Göthite occurs crystallised, scaly and fibrous, with a colour varying from rust-yellow to black. Formula, Fe_2O_3, H_2O. It contains 63 per cent. iron when pure. *Limonite, or brown iron ore*, is compact and earthy. Formula, $2Fe_2O_3, 3H_2O$. Bog ore is also a brown hæmatite.

Spathic Iron Ore, Siderite, Clay Ironstone, Blackband, and Cleveland Ironstone are different varieties of the carbonate of iron ($FeCO_3$). This class is the chief source of British iron. *Siderite* when pure yields 48·27 per cent. of iron. It varies in colour from yellow to brown, and has a pearly lustre. It often contains oxide of manganese, and this when smelted produces "spiegel-eisen." It gives a white streak. *Clay ironstone* is the carbonate mixed with clay, and *blackband* is the same compound containing bituminous matter. *Cleveland ironstone* is a less pure variety of clay ironstone, containing a large quantity of phosphates.

The following table shows typical composition of different ores of iron :

Name. Locality.	Magnetic Iron Ore. Danne-mora.	Red Hæmatite. Ulver-stone.	Brown Iron Ore. Dean Forest.	Spathic Ore. Brendon, Somerset-shire.	Clay Ironstones. Black-band, Lowmoor.	Clay Ironstones. Dudley.	Cleveland Ore. Eston.
Ferric oxide (Fe_2O_3),	27·55	93·23	90·05	·81	1·45	·40	3·60
Ferrous oxide (FeO),	58·03	—	—	43·04	36·14	45·86	39·92
Manganese oxide (MnO),	·10	·23	·08	12·64	1·38	·96	·95
Alumina (Al_2O_3),	·29	·63	·14	·01	6·74	5·56	7·86
Lime (CaO),	·38	·05	·06	·28	2·70	1·37	7·44
Magnesia (MgO),	·61	—	·20	3·63	2·17	1·85	3·82
Potash (K_2O),	—	—	—	—	·65	—	·27
Silica (SiO_2),	12·54	4·90	·92	—	17·37	10·68	8·76
Carbon dioxide (CO_2),	·12	—	—	38·86	26·57	31·02	22·85
Phosphorus pentoxide (P_2O_5),	—	·09	·09	—	·34	·21	1·86
Sulphur trioxide (SO_3),	—	—	—	—	—	—	—
Sulphur,	·04	·03	—	—	·10	·10	·11
Iron pyrites (FeS_2),	·11	·56	8·22	·18	1·77	1·08	2·56
Water,	—	—	—	—	2·40	·90	—
Organic matter,	—	—	—	—	—	—	—

Iron Pyrites.—This mineral is very abundant in nature, and is only used as a source of iron after the sulphur has been removed in the manufacture of sulphuric acid, when the resulting oxide is known as " blue billy." The chemical formula is FeS_2. Some varieties are bronze-yellow in appearance, others are nearly white, with a metallic lustre; the streak is brownish-black, and the specific gravity varies from 4·8 to 5·1.

British Ores.—The chief ores of Britain are spathic ores and hæmatites, although magnetites and pyrites are present, the latter to a considerable extent in some localities. Clay ironstone occurs abundantly in Staffordshire, Yorkshire, Derbyshire, Warwickshire, Shropshire, North and South Wales, and Scotland ; blackband in Lanarkshire, Linlithgowshire, North Staffordshire, and South Wales; red hæmatite in North Lancashire, Cumberland, and North Wales; brown hæmatite in Gloucestershire, Glamorganshire, Northamptonshire, Leicestershire, Lincolnshire, Buckinghamshire, and Oxfordshire. Of the above ores hæmatite is valuable for producing pig iron for the Bessemer process on account of its comparative freedom from phosphorus and sulphur. It is also used as the cement in producing malleable cast iron, and as a fettling for puddling furnaces, etc.

Chemical Relations of Iron.—Pure iron may be obtained (1) by reducing pure ferric oxide in a porcelain tube by means of a current of hydrogen gas at 700° C. ; the iron is obtained in the form of a dark powder which fires spontaneously when moderately heated in air, forming ferric oxide. When the reduction is effected at a very high temperature a spongy mass of iron of a silvery grey colour is obtained, (2) by the electrolytic decomposition of a solution of pure ferrous chloride or sulphate, a white malleable mass of iron is obtained. Iron may be exposed to dry air for an indefinite period without alteration, but in the presence of moisture a layer of rust ($Fe_2O_3,3H_2O$) is formed. The oxidation is accelerated by the presence of carbonic acid, which is always present in the air, a carbonate of iron also being formed. This rapidly absorbs a further portion of water and oxygen from the air, and in this way the rusting is slowly conveyed to the centre of the mass of iron. The layer of oxide or carbonate is electro-negative with regard to iron, so that a galvanic action is set up, causing decomposition of the water. This electrical condition still further augments the liability of iron to rust.

When iron is strongly heated in contact with air or oxygen, its surface becomes rapidly coated with a scale of black oxide Fe_3O_4, which peels off when the iron is struck with a hammer.

Iron is readily attacked by hydrochloric or dilute sulphuric acid, hydrogen gas being evolved, and chloride or sulphate of iron being formed. If concentrated sulphuric acid be employed, the metal is oxidised at the expense of the acid, and sulphurous acid is evolved. If a clean strip of iron be immersed in fuming nitric acid the iron is not attacked, and is said to remain passive; if the temperature be raised, or the iron be touched with a copper wire, dissolution immediately begins. Ordinary nitric acid attacks iron vigorously, especially if slightly diluted, nitrate of iron being formed. Iron may be rendered passive to nitric acid by removing it from the liquid, exposing it to the atmosphere, and then re-immersing in the acid. The symbol for iron is Fe, and its atomic weight 56.

Iron and Oxygen.—There are three oxides of iron of metallurgical importance—ferrous oxide FeO, ferric or red oxide Fe_2O_3, and magnetic or black oxide Fe_3O_4. Ferrous oxide is a black unstable compound, which rapidly oxidises in contact with air, and unites with acids to form ferrous salts. This oxide is the principal base in all slags produced in refining pig iron, such as tap-cinder, $2FeO . SiO_2$. In combination with carbonic acid it forms that most important class of ores termed "spathic." Ferric oxide occurs in nature as hæmatite, and in the hydrated state as brown hæmatite. It is a stable compound, but in a white heat it gives up oxygen, forming the black oxide Fe_3O_4. The black or magnetic oxide is very abundant, forming the richest ore of iron. It is produced when iron is strongly heated in air or oxygen, and also by heating iron in contact with superheated steam, thus forming a protective coating. This is the principle of the Barff process.

Iron and Phosphorus unite direct at a red heat, forming phosphide of iron $Fe_{12}P$. When oxide of iron is reduced by carbon in presence of an earthy phosphate, phosphorus is separated and unites with the iron. Wrought iron containing ·3 per cent. of phosphorus is not much affected in tenacity, but is harder; ·5 per cent. makes it cold-short, but not red-short, and 1 per cent. makes it very brittle. The general effect of phosphorus on iron is to impart a coarsely crystalline structure, diminish its strength, increase its fusibility, and render it cold-short. The presence of phos-

phorus in cast iron diminishes its strength, but such iron, on account of its fusibility, is useful in making fine castings.

Iron and Arsenic readily unite when heated together. Arsenic makes iron red-short and brittle.

Iron and Sulphur when heated together combine to form sulphide of iron FeS. The effect of sulphur, even in small quantities, is very injurious to wrought iron, making it red-short, although the metal may be worked in the cold. With cast iron, sulphur is often an advantage, making it stronger, more easily fusible, and more liquid when melted. Sulphur in pig iron leads to the production of the white variety, and the fractured surface often exhibits black patches. Ferrous sulphide is little affected when heated alone with carbon, but when roasted in an oxidising atmosphere at a moderate temperature it is converted into ferrous sulphate, while at a high temperature it is decomposed, forming ferric oxide and sulphur dioxide.
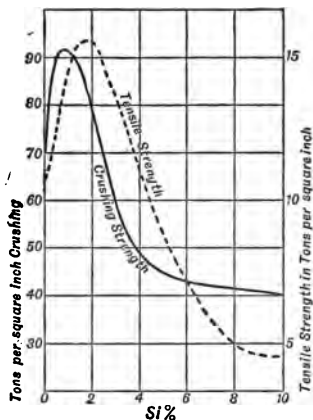
Fig. 30A.

Iron and Silicon combine to form silicon iron, which is white and highly crystalline. When iron is strongly heated in contact with silica and carbon, the silica is reduced to silicon, which unites with the iron. The effect of silicon on cast iron is to set the confined carbon free, so that, as a rule, the greyer the pig the higher is the amount of silicon present. Silicon makes wrought iron hard and more fusible.* The action of silicon on pig iron in modifying the tensile and crushing strengths is shown in Fig. 30A.

The slags produced in purifying pig iron consist chiefly of basic silicate of iron ($2FeO,SiO_2$). When this silicate is heated with access of air for some time, and then the temperature considerably increased, a very refractory substance is formed called "bull-dog," consisting largely of oxide of iron, and an acid fusible silicate liquates out, called "bull-

* See Turner's Researches, *Journal Chem. Soc.* 1885.

dog slag." The above oxide does not unite with silica when heated, but if carbon or a reducing agent be present, it may be reduced to ferrous oxide, FeO, which then unites with the silica.

Iron and Carbon.—Carbon unites with iron in various proportions up to about $4\frac{1}{2}$ per cent., forming the different varieties of steel and pig iron. When manganese is present a larger proportion of carbon may be taken up, but silicon and sulphur tend to lower the saturation point of carbon. The difference between malleable iron, steel, and pig iron is chiefly dependent on the relative amounts of carbon in combination with the iron. The more the carbon, the harder and more fusible the metal becomes, and this effect is considerably increased by the presence of other bodies, such as phosphorus, sulphur, etc. Combination takes place when iron is heated in contact with gaseous fuel, such as carbonic oxide, cyanogen, and hydrocarbons ; or by a prolonged exposure to a high temperature in contact with solid carbon, such an operation being termed cementation. When the carbon present in iron exceeds ·25 per cent., the iron is sensibly harder : this may be considered the greatest amount of carbon which can be present in malleable iron without diminishing its softness and malleability. Steel may be considered as iron containing from ·25 to 1·8 per cent. of carbon. When the proportion of carbon is low the metal is termed "mild steel" or ingot iron, and in like manner those with the higher proportions of carbon are termed "hard steels." Carbon exists in pig iron in two states—free and combined. When the carbon is chiefly in the combined form, the iron is "white." On the other hand, when the carbon is free, being diffused through the iron in crystalline scales, the iron is termed "grey"; but neither variety is entirely free from graphite or combined carbon respectively. In some varieties the carbon is partly combined and partly free, which gives to the fractured surface of the metal a speckled appearance, consisting of grey spots, enclosed by reticulating lines of white : it is then termed "mottled iron."

The amount of carbon in the combined form may be readily determined by Eggertz's method, which depends on the fact that, when iron or steel is dissolved in nitric acid, the intensity of the colour of the solution will be proportional to the amount of carbon originally present in the combined form. The graphite, not being affected by nitric acid, will remain in the insoluble residue.

Grey pig iron may be converted into white, by melting and sudden cooling, the iron being considerably hardened by this means. This principle is applied in chill casting. *Vice versa*, white iron is changed to grey by melting and slow cooling. From the above remarks it will be observed that grey pig iron is much softer than white, and the hardness of hardened steel may be due to the carbon passing into the soluble form, while annealing restores it to the non-hardening condition.

PROPERTIES OF MALLEABLE IRON.

Malleable iron is of a greyish-white colour, having a granular, crystalline, or fibrous fracture, according to the mode of treatment. When rolled or hammered hot the iron becomes fibrous, but continued cold hammering induces a crystalline or granular structure, making it hard and brittle. The nature of the fractured surface varies also with the manner in which the iron has been broken, for specimens broken by progressively increasing stresses are invariably fibrous, whilst the same specimen broken by a sudden blow will be crystalline. The presence of impurities generally tends to impart a granular or crystalline fracture, and makes the iron less malleable. When impurities, such as sulphur and arsenic, render the metal unworkable at a red heat, it is said to be hot or red-short. On the other hand, some substances, such as phosphorus, cause iron to crack when hammered cold, it is then termed cold-short. The specific gravity of iron is about 7·9, and when the metal is compressed at a high temperature, the density is increased ; but in wire-drawing and cold-rolling the metal elongates more than its transverse section diminishes, and the density is diminished, but its tenacity is increased. Its fusing point is said to be about 1600° C. ; but before melting it assumes a pasty state, when two pieces may be joined together by welding. To ensure a good weld the surfaces must be clean, and the metal at a white heat. In order to dissolve any scale the smith adds a little sand, which unites with the oxide and forms a fusible silicate. The presence of any foreign bodies, such as carbon, silicon, sulphur, phosphorus, copper, oxygen, etc., increases the difficulty of welding. Iron possesses considerable malleability, ductility, and tenacity. Its tensile strength ranges from 17 to 25 tons per square inch, but this, like all the other physical properties,

is modified by the presence of impurities, which tend to make it harder, more fusible, and brittle. When iron is heated to dazzling whiteness, it burns, forming the black oxide Fe_3O_4, the iron becoming friable and brittle, and is then termed "burnt iron." Iron may be magnetised by bringing it in contact with, or near to a magnet, but it loses its magnetism when the exciting magnet is withdrawn. Its specific heat is ·110, and its conductivity about 120, silver being taken as 1000. Its electric resistance is 5·8 times that of pure copper. When iron is exposed to moist air it readily rusts or oxidises, so that it is often coated with some substance to prevent this action, such as tinning, galvanising, and painting.

DIRECT METHODS OF EXTRACTING IRON.

Two distinct methods are employed for smelting iron ores, known respectively as the "direct" and "indirect" methods : the former, which is the older and little used at the present time, has been superseded by the latter or more modern method. The various processes are represented in a general manner in the accompanying scheme (Fig. 31).

In the *direct method*, the ore is reduced to iron or steel, in arrangements such as the Catalan forge and Siemens's rotator, then hammered, re-heated, and finished with the hammer or rolls. In the *indirect method*, the ore is calcined, and afterwards reduced in a blast furnace, the iron then being run into pig moulds ; the pig iron so obtained is afterwards puddled, hammered, rolled, re-heated, and finished in the rolls for bar iron. If steel is desired, the bars are heated with carbon in the cementation furnace, then melted in crucibles for cast steel.

In the old method, the finery and open fire were used instead of the puddling and re-heating furnaces.

Pig iron is treated in the Bessemer converter for the production of Bessemer steel ; in the Siemens furnace for Siemens steel ; and melted in the cupola for foundry purposes. The bloom of iron produced in the rotatory furnace was made into steel by treating it in the Siemens open-hearth furnace.

When malleable iron is extracted from the ore in one operation the process is said to be "direct." Many attempts have been made in recent years to revive the ancient principle of direct extraction, but the blast furnace has been

Fig. 31.
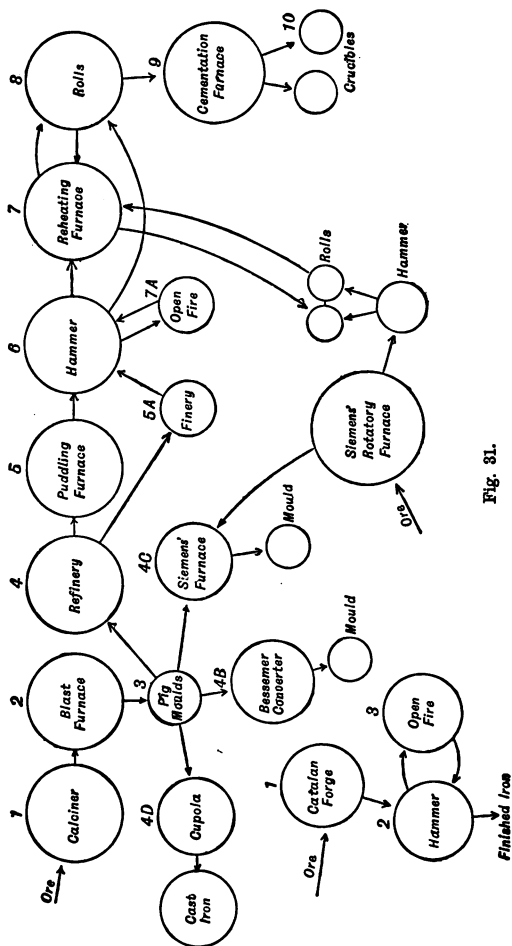
brought to such a pitch of excellence as regards economy of materials, and perfection of its reducing action, as to outstrip all rivals.

In reducing the ore direct, two things have to be taken into account : 1st, the easy oxidation of iron by carbon dioxide and water, at the temperature at which ferrous oxide is reduced to the metallic state by carbon, carbonic oxide, or hydrogen ; 2nd, the facility with which iron at a red heat combines with carbon. Now if gaseous fuel be employed as a source of heat and reducing energy, carbon dioxide and water would be produced, and a large excess of unburnt gas would be required to neutralise the oxidising tendency of these bodies, and this excess would require to be increased with the temperature. Sir L. Bell states that at a temperature near whiteness, iron will be oxidised, if carbon dioxide and carbonic oxide are present in equal proportions, and that when the volume of carbon dioxide CO_2, to carbonic oxide CO, is as 11 to 100, the reduction of protoxide of iron is no longer possible. In other words, gas ceases to be useful as a reducing agent when it contains one-tenth its volume of burnt gas (CO_2). The enormous volume of unburnt gas not only represents a great waste of fuel, but also a great quantity of heat is absorbed in raising it to the requisite temperature, which can only be done by strongly heating the whole of the gas previous to its partial combustion. In the blast furnace the combustion of solid carbon to carbonic oxide produces the requisite temperature, without producing an oxidising atmosphere, which makes that furnace unequalled for reducing energy.

With regard to the second difficulty, viz., the readiness with which iron combines with carbon at a red heat. If solid carbon be employed to reduce oxide of iron, then only the exact quantity of carbon for such reduction must be added, in order to avoid carbonisation of the iron, and the operation must be performed in a closed vessel heated from the outside. But for this purpose the ore must be broken small, the flux and fuel well mixed with it, and the temperature maintained for a long time, with a considerable expenditure of fuel.

In all direct processes malleable iron can only be produced by sacrificing a considerable portion of the iron, which passes into the slag, and this loss is in inverse ratio to the amount of carbon taken up by the iron. On the other hand, the blast furnace allows of the most perfect

utilisation of the fuel, and the slags produced therein are practically free from iron. Moreover, the pig iron produced can be converted into malleable iron or steel in the Bessemer converter, without an additional expenditure of fuel.

Fig. 32.

Catalan Process.— This primitive method of making iron is now practically obsolete, only being retained in remote districts where there is an abundant supply of wood fuel and rich ores, as in the Pyrenees. It consists of a hearth made of sandstone, and lined with charcoal (Fig. 32). The back and opposite walls are faced with iron, and of the remaining sides, one is of rough masonry, and the other, which forms the working side of the furnace, consists of two iron plates, the lower one having a hole for tapping the slag. The top of this plate serves as a fulcrum for the workman's tools. The twyer is made of sheet copper, and generally inclines at an angle of from 30 to 40 degrees, according to the degree of carbonisation desired. The blast is supplied by a blowing apparatus called a trompe (Fig. 33). The water falling down the pipe A, drags air through the inclined openings BB. This mixture of air and water falling into the cistern is divided into two streams, the air rising and passing forward into the twyer at a pressure of 1½ to 2 lbs. per square inch, the water running out of the cistern at C.
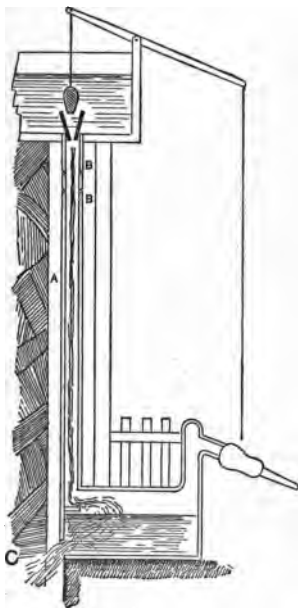
Fig. 33.

American Bloomery, Jersey—and Champlain Forge.—This simple method, largely employed in the United States and Canada, is a

modified form of the Catalan process, and is conducted in much the same manner, except that the ore is in a finer state of division, and the furnace is worked continuously.

The furnaces are built in rows on either side of a wall, each measuring about 28 by 30 inches in area by 25 inches in height above the twyers, and 14 inches below them. The sides are formed with cast-iron plates, and the bottom of beaten earth or cinders. In some cases a hollow iron bottom, cooled by water, is used. A water-box, 12 inches by 8 inches, is let into the twyer plate, and the water, after cooling the twyer, passes through the bottom plate. The twyers are arranged so that the blast strikes the middle of the hearth. In front of the forge, at 16 inches above the bottom, is a flat iron hearth, 18 inches wide, and in the side plate beneath it is a tap-hole for withdrawing the slag. The blast is used at a pressure of $1\frac{1}{2}$ to $1\frac{3}{4}$ lbs. per square inch, and heated to 300° C. by passing through cast-iron pipes in chambers fixed above the hearth.

Chenot Process.—This was introduced about the year 1855, but was soon abandoned except in one locality in Spain, where its continuance depended on the possession of a quantity of charcoal screenings, which would otherwise have been wasted. The reducing furnaces are rectangular retorts, built in pairs, and heated externally by coal fires, the flames from which circulate round both retorts by suitable channels. Four tons of fuel are required for the production of one ton of iron, and about 45 per cent. of iron is lost. The charge consists of ore and charcoal. The reduction and cooling of the sponge of iron extends over three days, the yield being 15 cwts. of iron per 24 hours.

In 1873 Mr. Blair, in America, introduced the Chenot process on an improved plan, but the furnace was irregular in its action, and the production small compared with that of the blast furnace. The retorts are cylinders 3 to 4 feet in diameter, and 40 feet high. The great difficulty was to cause the heat to penetrate successfully to the centre. In order to effect this, Blair placed in the top of each retort a concentric cylinder, and through its axis a double blowpipe, by means of which a current of gas and air was forced in, producing by its combustion sufficient heat to make the ore and charcoal, charged into the annular space round the cylinder, red-hot.

Fig. 34 represents in section and plan one of a group of three furnaces. A is the retort, C the cylinder, D the gas pipe, E the air pipe, F the charging space, G the annular

space for combustion of the gas, K the gas main which introduces the gas at two different levels. This gas was originally obtained from the reduction of the ore, but its amount being found insufficient, a special gas producer was afterwards provided. The cylinder L beneath the reduction chamber receives the sponge of iron, and is kept hermetically closed while the iron cools, as in the Chenot furnace. The wrought-iron walls are double, in order to allow a current of water to circulate through them.
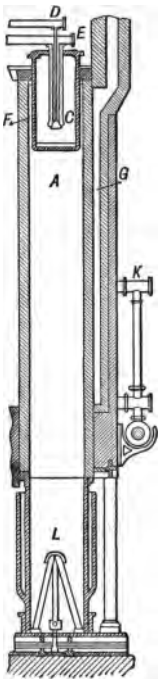
Husgafvel's High Bloomery is one of the most successful furnaces for the direct method yet devised. It is a tall shaft furnace, with double air-cooled iron walls and movable hearth. The air space between the double walls serves for heating the blast. The lower 5 feet of the shaft are lined with firebrick. The movable hearth has four water-cooled twyer holes, and is provided with a false bottom, so that accretions may not form on the true bottom. Crushed ore and slags with charcoal are charged into the shaft, and the burden descending, gradually reaches the hearth quite reduced, and probably carburetted. The bloom of metal is removed along with the hearth, and a fresh hearth immediately fixed in position. The slag is tapped at intervals.
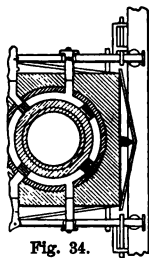
Siemens Direct Process.—This is another of the somewhat recent attempts to extract iron in an economical manner from the ore in one operation, but it suffers under the disadvantages of all direct methods, as explained on page 125.

The furnace (Fig. 35) consists of a cylindrical rotating chamber, $10\frac{1}{2}$ feet in diameter and about the same in length, and rests on four anti-friction rollers. The inside is lined with bauxite, which consists of alumina, ferric oxide, water, and a little silica. From this substance, when mixed with 3 per cent. clay and 6 per cent. plumbago, bricks are

Fig. 34.

made. The working door is at one end, and beneath this is a tap-hole for slag. The furnace is heated with gas supplied from a gas producer, the air being heated by passing through one of a pair of regenerators. Ore in small pieces is charged into the hot furnace with lime, and the cylinder rotated. When red-hot, about 20 per cent. of small coal is added as the reducing agent, and the velocity increased. The carbon and hydrogen of the coal, together with the carbonic oxide of the gas, react on the oxide of iron, removing its oxygen and liberating metallic iron, the particles of which gradually cohere to form a spongy mass, called a bloom. The lime and some of the basic lining of the furnace unite with the
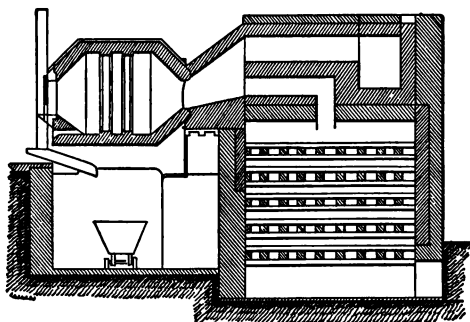
Fig. 85.

siliceous matters to form a slag, which, in consequence of its basic character, is highly favourable to the taking up of any phosphorus that may be present in the ore. When the reduction is complete the slag is tapped off; then a quick rotation is imparted to collect the iron into three or more balls, which is effected by means of ribs projecting from the lining. The balls are then shingled, re-heated, and finished in the usual way. If steel is desired, 10 per cent. of spiegel-eisen is added after tapping off the slag. The charge is then melted and cast into moulds. In some cases the balls are treated for steel in the open-hearth furnace. The advantages claimed for this method are—economy of time, saving of fuel, and purity of the iron, since the metal is not brought in contact with solid fuel, as in the blast furnace, except the coal added as a reducing agent.

I

PIG IRON. PREPARATION OF ORES.

Pig or Cast Iron.—In the indirect method of producing malleable iron, a crude product consisting of iron, carbon, silicon, phosphorus, sulphur, manganese, and very frequently other elements, such as copper, arsenic, titanium, chromium, etc., is first obtained ; it is termed "pig iron," and is D-shaped in section, being 3 or 4 inches square and about 3 feet long. Pig iron is arranged into a variety of classes, according to the colour, texture, size of the crystalline plates, and general character of the fractured surface. That containing the largest grain and largest crystals of graphite is known as No. 1, the numbers increasing as the lustre and size of the grain diminish. When the metal ceases to be grey the numbers are not used, the iron being designated as mottled, either strong or weak, and white, in which, when manganese is present in quantity, the crystals are large and lustrous and the iron intensely hard ; such a pig is termed spiegel-eisen. The lower numbers of grey iron are called foundry pigs, being used for castings. The higher numbers are termed forge pigs, being chiefly used for the production of wrought iron. Two other varieties are also made, which, owing to their comparative freedom from sulphur and phosphorus, are used for making Bessemer steel, and are termed Nos. 1 and 2 Bessemer pigs.

Grey iron requires a higher temperature to melt it than white iron, but becomes very liquid, and expands on becoming solid, which admirably adapts it for casting. White iron becomes less perfectly fluid and passes through an intermediate pasty stage before becoming liquid, and the same during solidification after fusion. It contracts considerably after becoming solid. Grey iron is produced at a higher temperature in the blast furnace than white, which tends to make it more impure. It sometimes happens that both kinds are contained in the hearth of a blast-furnace at the same time ; the white being the heavier goes to the bottom, and when the furnace is tapped flows out first in a sluggish stream, emitting brilliant sparks ; the grey iron following runs perfectly fluid without sparks.

Common white iron is produced when the furnace is charged with a heavy burden of cinders, *i.e.* slag from other processes mixed with ore, and is then termed "cinder pig," as distinguished from metal produced from ore alone, which is termed "all-mine pig." Cinder pig is dull in colour, and

presents a rough honeycombed appearance on the surface; it is very hard and brittle. White iron is also produced when easily reducible ores are employed, so that the charge can be reduced and melted rapidly, and the melted metal remain a shorter time in contact with the highly heated carbon. In such a case a greater proportion of ore to fuel is employed, and consequently a lower temperature obtained. The production of grey iron requires a temperature far beyond that of mere fusion, causing the reduction also of other oxides, such as silica, besides those of iron. Such a condition is brought about by working with light burdens, that is, excess of fuel, and using very hot blast. Other things being equal, the iron will be grey if the slag is refractory, for the particles of carburetted metal cannot coalesce until the foreign matter has united with the flux to form a fusible slag, hence they remain longer subjected to the action of carbon and silicon, which latter element induces greyness in pig iron. The following analyses show the composition of (I.) grey, (II.) white, (III.) spiegel-eisen, (IV.) mottled pig iron:

	I.	II.	III.	IV.
Iron, . . .	94·56	94·08	88·84	94·56
Graphite, . .	3·10	·10	·12	1·50
Combined carbon, .	·04	3·00	3·17	1·64
Manganese, . .	·50	1·37	7·39	·50
Other constituents, .	1·80	1·45	·48	1·80
	100	100	100	100

PREPARATION OF IRON ORES FOR SMELTING.

Iron ores are sometimes subjected to preliminary operations preparatory to the smelting process, according to their nature and to the facility of obtaining supplies. In parts of the world where good ores are abundant, such as in England, mechanical treatment of poor ores, such as washing, dressing, etc., offers no advantages. On some parts of the Continent, where the opposite condition holds, poor ores are sifted, crushed or stamped, and washed, in order to remove lighter impurities, such as sand, clay, etc.

For regularity of result in smelting, it is advisable to have the lumps of ore, fuel, and flux reduced to a uniform size, according to the capacity of the furnace, and the greater or less ease with which the ore is reduced. In the large Cleveland furnaces blocks of ore 4 to 6 inches in diameter are

employed, while the hard magnetic ores of Sweden are reduced to ¾ or 1 inch cubes. Large pieces allow a freer passage for the gases ; small pieces pack closer and offer greater resistance to the blast, but a greater surface is exposed to the reducing gases.

Weathering.—In some cases, such as the clay iron-stones of the coal measures and ores containing pyrites, exposure to the atmosphere for a lengthened period causes oxidation and disintegration of the shale and pyrites, whereby the former can be readily separated, and the latter are partially oxidised and washed away by water.

Calcination.—This operation is resorted to in the case of all iron ores, except massive red hæmatite and certain magnetites. The effect of this is to decompose any pyrites, with the partial volatilisation of the sulphur, to eliminate carbonic acid, water, and other volatile matter, and to convert ferrous into ferric and magnetic oxides, which greatly reduces the liability to form slag with silica. Moreover the ore is rendered more porous, and more readily susceptible to the action of reducing agents. The loss of weight by calcination is from 25 to 50 per cent.
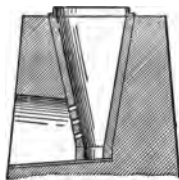
Fig. 36.

Calcination is performed in heaps, in stalls, and in kilns. The first method is adopted in localities where fuel is cheap and space abundant. The ground is first covered with a layer of coal a few inches thick, then a layer of iron ore 12 inches thick ; this is succeeded by fresh layers of coal and ore, the whole heap being from 3 to 9 feet high. Fire is then applied at the base, and the combustion gradually extends to the whole mass: 3 cwts. of coal being required for 1 ton of ore. Blackband ironstone often contains sufficient carbon to effect the calcination without additional fuel, except the layer of small coal at the base.

Calcination is conducted in some districts in stalls, each of which consists of three vertical walls enclosing a space into which the ore is placed. Draught holes are left at suitable intervals for the passage of the air. This forms a kind of rough kiln. Calcining in kilns is much preferable to the preceding method, as the fuel is more perfectly utilised and a more uniform product is obtained. In South Wales the kiln (Fig. 36) is in the form of an inverted truncated cone in section, 15 to 18 feet high, 20 feet long, 8 to 9 feet wide at

top, and 2 feet wide at the base. Two arched passages, splayed outwards, are left at the base for withdrawing the charge. At a height of a few feet above the top is a railroad supported on pillars, over which the loaded wagons pass, and deliver their contents into the kiln in alternate layers of ore and fuel.

One of the best forms of kiln is that of Gjers (Fig. 37), largely used in the Cleveland district. The body is of fire-brick cased with wrought-iron plates. The diameter at base is about 14 feet, at the boshes about 20 feet, and at the top about 18 feet. The bottom of the brickwork rests on cast-iron plates, and the whole is supported on cast-iron pillars. In the centre of the base of the kiln is a cone about 8 feet high, and the same in diameter at the base. The total height of the kiln is about 30 feet, and the capacity about 6000 cubic feet. From two to three days are required for the calcination, with the consumption of 1 cwt. of coal per ton of ore. When the operation is complete, the ore is dis-charged at the bottom between the pillars, being directed outwards by the cone. The calcination is carried on continuously.

Fig. 37.

Fig. 38 represents a Swedish kiln about 20 feet high, employing the waste gases of the blast-furnace as a source of heat, instead of solid fuel. The com-bustion is effected by means of a blast of air introduced through the twyer (a), which communi-

Fig. 38.

cates with the annular space (b), from which the air penetrates into the furnace by a number of small open-ings. The gas is conveyed by the pipes (dd), and enters
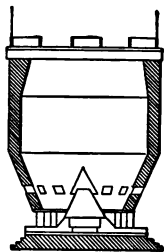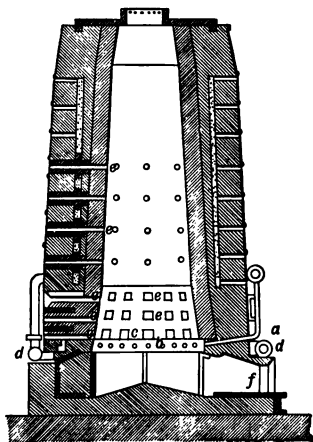
the furnace by the channels (*e*). Above these are other
channels (*ee*) which are kept closed ; these are used for in-
troducing bars to break up any lumps that may have caked
together, or to admit additional air if necessary. The cal-
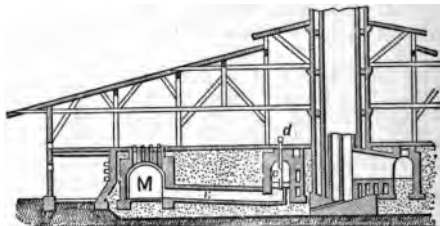
Fig. 39.
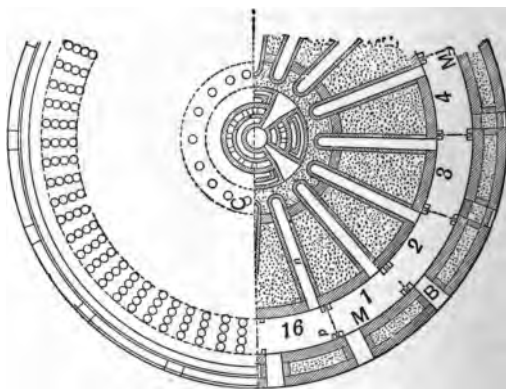
Fig. 40.

cined ore is discharged through five radial openings (*f*).
The charging is performed at the top, which is surmounted
by a chimney for regulating the draught.

Hoffmann's calciner is designed to utilise the whole of the
heat generated by the combustion of the fuel, thereby
effecting a considerable saving. It differs from a shaft fur-
nace with regard to the direction of the gaseous current, and
the stationary condition of the solid matter. The com-
bustion is conducted in a horizontal direction in the same
order as the gas. Figs. 39 and 40 represent a circular

furnace of this kind in section and plan. The calcining space is circular, and is roughly divided into sixteen compartments (MM) by means of projections raised towards the roof. The whole circular space is divided by means of a wrought-iron door (P). In Fig. 40 this door divides No. 16 from No. 1 compartment. A lateral opening or doorway (B) is also provided for each chamber, for the purpose of discharging the calcined ore, but it is bricked up during the operation, only two being open at a time—one being charged and the other being discharged. The air for combustion is drawn through these doorways, and passes in the direction of the chambers 3, 4, 5, 6, etc. Each compartment communicates with the central gallery (c), and thus with the chimney by means of inclined flues (n), each of which is provided with a damper (d); all these are kept closed, except that connected with No. 16. Along this flue the products of combustion finally pass into an interior circular space (c), termed the smoke flue, which communicates with the chimney. The outer wall is double, about 3 feet thick, the two portions being separated by a space filled with sand, in order to close up any cracks produced by heat in the brickwork.

The cold air, as before mentioned, passes into the calciner at Nos. 1 and 2, then circulates through 3, 4, and 5, containing ore already calcined, the air being heated at its expense. The air then arrives at No. 6, where the ore is red-hot. The fire commences here and occupies No. 7 and part of No. 8. This is the zone of greatest heat. The gases then traverse the remaining chambers, giving up their heat to the matter being calcined.

The fuel is charged in small quantities through openings in the roof, when it inflames immediately, and burns without smoke, because of the high temperature of the air employed for its combustion, and the incandescent space into which it arrives. The same openings are only used for charging every twenty-four hours, a fresh range being opened every four hours, working in the direction of the general current. Every twenty-four hours the operation in one chamber is completed. Then the iron partition (P) is transferred from No. 1 to No. 2, the doorway of No. 1 closed and that of No. 3 opened. The damper of No. 16 is then closed and that of No. 1 opened. Now the contents of No. 3 are discharged and the chamber No. 2 re-filled. The operation is thus continuous, and only stopped in the case of serious repairs. This furnace is chiefly used for baking bricks and burning limestone. An oval form is also employed in some works.

CHAPTER IX.

INDIRECT METHOD OF EXTRACTION.

Reduction in the Blast Furnace.—The calcined ore is put into the blast furnace with coal, coke, or charcoal, and a suitable flux, which is usually limestone. The heat is well utilised, and the reduction more perfect than in any other form of furnace. In the blast furnace there are two currents travelling in opposite directions, and constantly acting on each other—a " gaseous " ascending current and a " solid " descending one. The former travels at the rate of about 3 feet per second, and the latter at the rate of 3 feet per hour. The effect of the blast on the carbon of the fuel is to produce carbon dioxide CO_2 at the level of the twyers, with the evolution of great heat. This gas ascends, and is reduced by carbon at a very short distance from the twyers, thus :

$$CO_2 + C = 2CO.$$
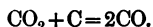
This carbonic oxide is the principal reducing agent in the blast furnace, the oxide of iron being reduced to the metallic state as a spongy mass, thus :

$$Fe_2O_3 + 3CO = 3CO_2 + 2Fe.$$
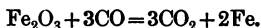
At the same time the flux, the earthy matter of the ore, unite to form slag, which descends with the iron ; the latter in contact with highly heated carbon is carburised, then melts and collects in the hearth, where, in combination with other substances, such as silicon, phosphorus, sulphur, and manganese, which have also been reduced, it constitutes pig iron. On the top of the molten iron floats the liquid slag. The temperature and pressure have a great influence on the reducing action, and as the temperature increases with the temperature and pressure of the blast, it follows that as the reducing energy becomes greater the metal is more impure.

When very pure iron is desired, rich hæmatite and cold-blast are used, with charcoal as fuel. Great advantage is gained by the use of hot air, as less carbon is required for reduction and fusion. It is also useful to remedy defects, and to regulate the passage of materials in the furnace. If the fusion or reduction is at fault the temperature of the blast is raised, or more fuel is added. The former acts instantly, while the latter often takes several hours to remedy the defect.

The quality of the pig iron produced from a given furnace will depend on the temperature, the nature of the charge, and the mode of working. With easily reducible ores and heavy burdens—that is, with a large proportion of ore to fuel—the iron will be white, since the metal is kept only the minimum time in contact with incandescent carbon. With a high temperature and a light burden the pig iron is more siliceous and grey. The same things influence the character of the slag. Blast furnace slags are mainly double silicates of lime and alumina, and may be represented by the formula

$$3(CaO.SiO_2) + Al_2O_3.3SiO_2,$$
or $$6(2CaO.SiO_2) + 2Al_2O_3.3SiO_2.$$
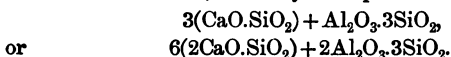
The former is the kind of slag obtained from charcoal furnaces, and the latter from furnaces using coke or coal. In both cases the lime is replaced more or less by magnesia, oxide of iron, and oxide of manganese; while the silica is sometimes replaced to a small extent by alumina. The colour varies from white to grey, sometimes with varying shades of yellow, green, blue, and black, according to the metallic oxides present. Generally a white or grey slag accompanies grey iron, and a dark-coloured slag, white iron. The former slag often contains excess of lime, which diminishes its fusibility; the latter is more fusible, and contains oxide of iron, which, when present in quantity, makes a very liquid "scouring" slag, *i.e.* one attacking the lining of a furnace. The "scouring" slag sometimes contains as much as 20 per cent. of iron. When forge or mill cinders are added to the charge, the resulting metal is called cinder pig iron, and the change produced by the reduction of such slags may be represented by the following equation :

$$3(2FeO.SiO_2) + 4C = (2FeO.3SiO_2) + 4CO + 4Fe.$$
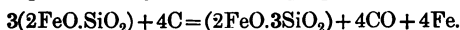
When phosphorous pentoxide P_2O_5 is present in the blast furnace it is reduced, and the phosphorus passes into the iron, but this can be prevented by allowing much oxide of iron to

pass into the slag. Blast-furnace slag has been utilised for building purposes, and for making slag wool.

The temperature and condition of the charge in different parts of a blast furnace are represented by the aid of Fig. 41, prepared by Sir L. Bell. The zone (a) contains the raw materials ; in (b) the ore is partially reduced by carbon ; and in (e), which is at a dull red heat, the limestone added as a flux is decomposed into lime CaO, and carbon dioxide CO_2, which is liberated, thus :

$$CaCO_3 = CaO + CO_2.$$

In the zone (e) carbonic acid CO_2 oxidises carbon from the fuel forming carbonic oxide CO ; and in (f), which is at a bright red heat, the reduced iron takes up carbon, forming pig iron. This action is continued in the lower zones, in which foreign oxides, such as silica and phosphoric acid, are also reduced, the silicon, phosphorus, etc., uniting with the iron. In the zone (i) the temperature is very high and the iron is thoroughly fused, as well as the slag formed by the union of the flux with the earthy matter. In the zone (k) the temperature attains to intense whiteness ; here the molten materials separate according to their specific gravities, the iron falling to the bottom, and the lighter slag floating on the top.
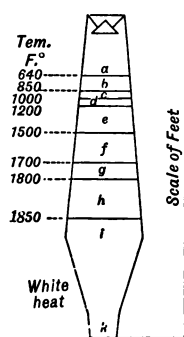
Fig. 41.

* Carbonic oxide never completely reduces oxide of iron, and at high temperatures it even oxidises iron, especially if in the spongy form. Carbon dioxide oxidises hot iron energetically, and if in sufficient excess will probably produce ferric oxide. These actions are shown in the following equations :

(1) $Fe + xCO = FeOx + xC.$
(2) $Fe + xCO_2 = FeOx + xCO$
(3) $FeOx + yCO_2 = FeOx + y + yCO.$
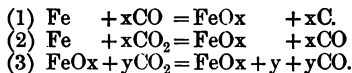
If, then, iron, oxygen, and carbon, however initially combined, are exposed to a high temperature, the oxygen tends to distribute itself, according to the conditions required for equilibrium, depending on the temperature, proportion of

* See Howe's *Steel*, p. 118.

iron to carbon, etc. It will be seen from equation (1) that when carbonic oxide oxidises iron, carbon is set free, but carbonic oxide may carbonise the oxygen of oxide of iron, forming carbon dioxide. This action is rapid between 400° and 450° C. These reactions are represented by the following equations:

(4) $FeOx + yCO = FeOx - y + yCO_2$.
(5) $FeOx + yCO = FeOx + y + yC$.
(6) $2CO = C + CO_2$
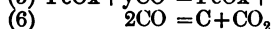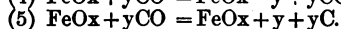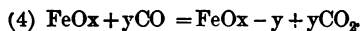
Under altered conditions, and especially at higher temperatures, deposited carbon is oxidised by carbon dioxide and iron oxide, thus:

(7) $CO_2 + C = 2CO$
(8) $FeOx + y + yC = FeOx + yCO$.
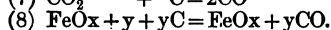
The action of carbon dioxide begins at 417° C., that of iron oxide at 265°. A mixture of 60 per cent. by volume of carbonic oxide, with 40 per cent. of carbon dioxide, still deposits a little carbon, but with 50 per cent. of carbon dioxide the deposition is completely arrested. It is to the deposition of carbon that we owe much of the carbon of cast iron, and also the removal of the last trace of the initial oxygen.

Dr. Alder Wright has investigated the chemical changes in the blast furnace, which may be represented by the following equations:

(1) $Fe_2O_3 + CO = 2FeO + CO_2$.
(2) $Fe_2O_3 + 3CO = 2Fe + 3CO_2$.
(3) $2Fe + 3CO_2 = Fe_2O_3 + 3CO$.
(4) $2FeO + CO_2 = Fe_2O_3 + CO$.
(5) $2Fe + 3CO = Fe_2O_3 + 3C$.
(6) $2FeO + CO = Fe_2O_3 + C$.
(7) $2Fe_2O_3 + C = CO_2 + 4FeO$.
(8) $2Fe_2O_3 + 3C = 3CO_2 + 4Fe$.
(9) $CO_2 + C = 2CO$.
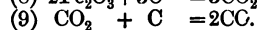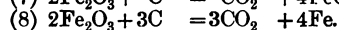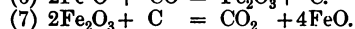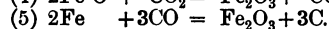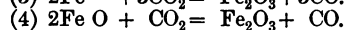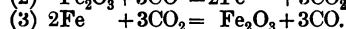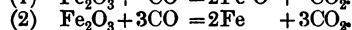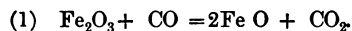
Thus equations 1, 2, 7, and 8 are reducing; 3 and 4 are oxidising; 5 and 6 are carbon reducing and iron oxidising. These changes may be proceeding simultaneously in a certain part of the blast furnace, so that the final effect will depend on the balancing of these opposing influences.

The Fluxes employed in iron smelting vary with the nature of the ore to be treated. In some rare cases the ores are self-fluxing, containing acid and basic constituents in the

requisite portions to form slag. This may be also effected by using a mixture of ores of dissimilar composition, such as siliceous or calcareous hæmatites, or both, with clay-ironstone. More generally a non-ferruginous flux is added, and although it increases the weight of material to be operated upon, it is more easily obtained.

For ironstone containing clay, which is very frequently the case, limestone is the flux used. Rich hæmatites, such as those of Cumberland and Lancashire, require clay as well as limestone. Of late years a brown hæmatite containing much free alumina, called "Belfast aluminous ore," has been used in preference to clay. Some smelters recommend the use of quicklime instead of limestone, thus effecting an economy of fuel, since the absorption of heat during the expulsion of carbon dioxide in the case of the raw carbonate, as well as the loss of carbon by the conversion of carbon dioxide into carbonic oxide, is avoided ; but it is necessary to use the lime soon after burning, otherwise it takes up carbon dioxide and moisture again from the air. When the ore is a carbonate, containing metals in the protoxide condition, the flux required is silica, added in sufficient quantity to form a silicate, in which the oxygen of the acid will be equal to the oxygen in the base, thus :

$$(2MO, SiO_2).$$
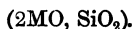
The Fuel used in a blast furnace is either charcoal, peat, coke, or raw coal. Charcoal is only used in small furnaces, on account of expense, but it is highly advantageous when very pure iron is required, owing to its freedom from sulphur and other impurities. Peat is only used in remote districts where other fuel is not available.

The value of coke for blast furnace work is largely dependent upon its comparative freedom from sulphur and ash. The coke must be sufficiently hard and dense to resist the great pressure of materials it has to sustain in large furnaces; on the other hand, it must be sufficiently porous to allow free passage for the ascending gases. Anthracite, notwithstanding its comparative purity, is very dense, and only permeable with difficulty ; it is also very liable to decrepitate into small fragments, which retard the draught. In South Wales, where this fuel is used, it is necessary to work with an open tymp, so as to clear out the small particles of anthracite from the hearth.

Raw coal is very largely used, both alone and in admixture with coke, which is probably the more advantageous method.

The coal employed must be of the non-caking variety; hence we find raw coal in use in the West of Scotland, Staffordshire, and Derbyshire.

Ferro-Manganese.—This may be considered a variety of pig iron in which the iron is replaced largely by manganese. It is produced by smelting, in the blast furnace, ores containing much manganese, and it is possible to obtain a product having as much as 87 per cent. of manganese. The furnace must be worked with a large excess of fuel; a large amount of limestone as flux so as to produce a basic slag; and a considerably greater pressure of blast, previously raised to a higher temperature than is used for ordinary iron ores.

Ferro-manganese is a hard, crystalline substance, but the crystals are much smaller than those in spiegel-eisen. It is chiefly used in steel-making by the Bessemer and open-hearth processes.

Blast Furnace and its Accessories.

An English blast furnace of the old type (Fig. 42) was a very massive structure of stonework or brickwork, usually circular in form in the interior, which consisted of a shaft approaching in sectional elevation to that of two truncated cones joined at their bases; the upper and more acute one being termed the "body," which was surmounted by a chimney containing one or more openings for the purpose of charging; the lower cone forming the "boshes." This lower cone was sometimes continued to the ground level, but more often the furnace was enlarged, forming the "hearth,"

Fig. 42.

in which the molten iron collected, three sides being continued to the bottom, and the other left open for means of access. The hearth was supported on a mass of masonry, with channels for the escape of moisture. The foundations were traversed by arched galleries in order to keep the whole building dry. One of the objects in the construction was to keep the heat as much as possible in that part where it was required, and to diminish loss of heat by radiation. The interior was lined with firebrick, and the outer part
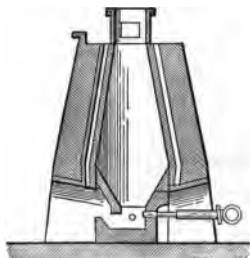
was built of rough sandstone or ordinary brickwork, the two layers being separated by a space filled with sand or slag. The dimensions varied in England from 9 to 20 feet in diameter, and 30 to 45 feet in height.

The modern blast furnace is an elongated barrel-shaped structure, the height being four to five times that of the greatest width. The body is formed of wrought-iron plates, ½ inch thick, riveted together, and within which is built the outer casing of ordinary masonry, the inside being lined with firebrick, about 18 inches thick, while in some cases between the two layers of brickwork is a small space filled with sand to allow for expansion and contraction. The body or stack is supported on a cast-iron ring resting on iron columns, and the lower part, from the top of the columns to the tymp arch, is also cased with iron. The hearth is independent of the masonry of the stack, and is built in after the stack is completed. It requires to be made of very refractory material of considerable thickness, having to withstand a very great heat in addition to the corrosive action of the molten slags.
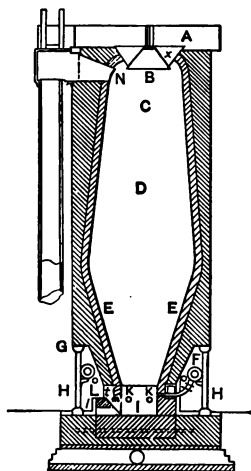
Fig. 43.

The hearth is perforated with three to six holes for the introduction of twyers, which convey the blast of air into the furnace. On the front or working side the hearth is extended outwards for a short distance, forming a rectangular cavity known as the fore-hearth, which is bounded in front by a refractory stone termed the dam-stone. The arch covering this cavity is called the tymp-arch. The tymp is made either of a block of refractory stone or of a hollow cast-iron box built in the masonry, and through this box a current of water constantly circulates in order to keep it cool.

In Fig. 43, A is the charging gallery, B is the cup and cone arrangement for charging, C the throat, D the body, EE the boshes, F the blast main, G the iron ring, and HH the pillars supporting the body, I the hearth, K the twyers, L the dam,

l the iron dam-plate, m the fore-hearth. The dam is formed of firebrick, and is carried up to the twyer level, a semi-circular notch in the top edge serving as a passage for the slag. The tap hole for the molten iron is a narrow slit through the bottom of the dam, t is the tymp, and N is the opening for conveying into the down-take pipe the waste gases, which are utilised for heating the blast, boilers, etc.

The charge is tipped into the cup or hopper x, and allowed to fall into the furnace by lowering the cone B, which acts very advantageously in distributing the charge over the sur-face of the materials already in the furnace.

Form and Interior Dimensions.—The descent of the materials must, in all cases, be sufficiently slow for the reducing action of the gas and carbon to penetrate to the centre of each fragment before it reaches the region of fusion, and, as a rule, the furnace is built smaller in proportion to the ease with which the various oxides are reduced.

The horizontal section given to the hearth must vary according to the pressure of the blast and the porosity of the materials employed in the fur-nace. When hard coke is used and the ore is in large pieces, a longer time is required for the gas to penetrate to the centre of each lump, and a greater pressure is then needed. But this tends to produce a higher temperature,

Fig. 44.   Fig. 45.

and, consequently, greater reducing energy, which neces-sarily makes the metal more impure. The height of the furnace should be limited when the fuel is friable, such as anthracite, and when the ore is in small pieces, for if the charge is too compact the gas can only circulate with difficulty. Moreover, in a mass of different materials, descending gradually, the effect of the difference of density becomes greater as the height of the furnace is greater ; the heavier pieces of ore tend to descend vertically while the lighter particles of fuel are forced to the sides, which circum-stance limits the possible height. The internal shape of a blast furnace should be that of the general form which it tends to assume after some weeks of working. It has been found in practice that the section has been modified where the heat has been greatest, and that the sharp angles of the hearth and boshes of the older forms were invariably burned away. When a furnace is working irregularly, which often
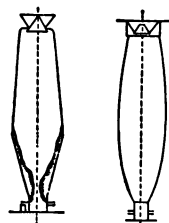
arises from an accumulation of lime and unreduced ore in the
hearth and boshes, it is generally due to scaffolding. Fig. 44
is a section of a furnace showing an excrescence of this kind,
given by Mr. R. Howson, who recommends the shape Fig. 45
as the best form for avoiding scaffolds. Greater height may
be given to a furnace to
increase its capacity, and to
intercept the heat more com-
pletely. Combustion should
only occur in the neighbour-
hood of the twyers, and the
greater the distance of the
upper end of the charge from
the zone of combustion, the
more perfectly will the heat
be extracted from the ascend-
ing gases, so that furnaces are
now built 80 to 90 feet in
height.
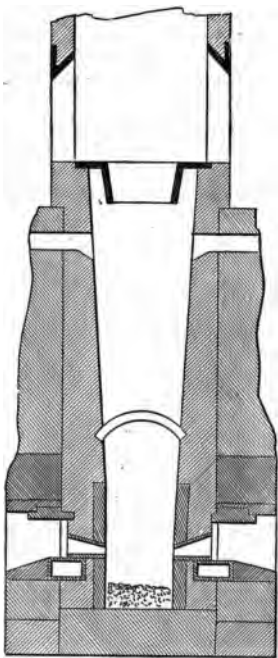
The section of most furnaces
is round, which economises
the heat, and causes it to be
more uniformly distributed;
but there is always a diffi-
culty in forcing the blast to
the centre, since the charges
sink more there than at the
circumference. This circum-
stance induced Rachette to
adopt an elliptical or rect-
angular section. The large
production of thirty tons of
grey iron in twenty-four
hours in this small furnace
is due to the suitable distri-
bution of the blast, and the
non-conducting nature of the
walls. Truman states that
the charges descend uniformly to the twyers, thus utilising
the fuel more completely, and that the smelting is rapid.
This furnace (Fig. 46) is oblong and rectangular in shape,
being 3 feet wide at the twyers, 7 feet at the throat, and
about 30 feet high, with a capacity of 2000 cubic feet. The
object of this shape is to keep the ascending gases more to the
centre, and to cause a more perfect action on the descending

Fig. 46.

solid materials. The blast is introduced through six or eight twyers, three or four being placed on each of the longer sides of the hearth, thus causing a better distribution of the air.

Collection of Waste Gases.—The waste gases of blast furnaces were formerly allowed to escape, the furnace tops being always left open; but this system has been almost universally abandoned, except in a few localities where fuel is cheap and cold blast is used.

Various contrivances have, from time to time, been devised for closing the throat, so as to prevent the escape of the waste gases, which are conducted into suitable apparatus, where they are burnt to generate heat for heating the blast, etc., as before mentioned.
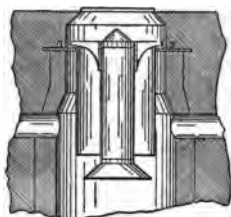
Fig. 47.

In the charcoal furnaces of Sweden, and some old coke furnaces, a portion of the gases is collected, without closing the top, by introducing a number of iron pipes through the brickwork, at a depth of 10 or 12 feet below the top. In the Upper Hartz and other places, an annular space is formed in the upper part of the masonry of the furnace, communicating with the interior, beneath the surface of the charge, by a number of openings inclining upwards, in order to prevent the lodgment of the charge in them. A large pipe opens into the annular space, and is connected with a high
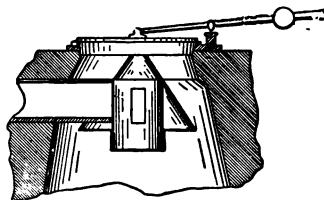
Fig. 48.

stack, so as to obtain the necessary draught for drawing off the gases. With some small straight furnaces a cast-iron cylinder is inserted in the throat, leaving an annular space which forms a collecting flue for the gases. The mode of charging by means of a central cylinder causes the more compact and finer particles to go to the centre and the larger pieces to the sides, which latter then become more permeable by the gases. In order to correct this defect a fixed cone (Fig. 47), supported by radial arms, is added, so as to distribute the charge more uniformly.

K

Escalle recommended a fixed cone without a cylinder (Fig. 48). The top being closed, the gas is collected by the cone, the radial arms which support it being hollow, so that the gases pass through them to the off-take. Movable cones are now more generally used, both for collecting the gases and distributing the charge. The most simple and general
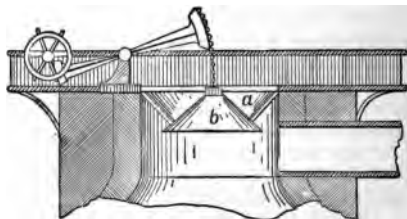
Fig. 49.

form consists of a fixed cup *a* (Fig. 49), and a movable cone *b* suspended by a chain, so that it may be raised or lowered at will. Various contrivances are in use for controlling the movement of the cone, a frequent form being a pinion moved by a hand-wheel, and gearing into a rack attached to a counterpoised weight. The gases pass through a lateral flue
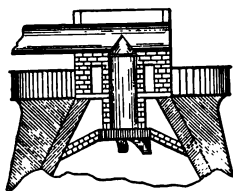
Fig. 50.

into the main pipe, which conducts them to the boilers, heating stove, etc. At Ulverstone, in Cumberland, a central iron tube (Fig. 50) lined with brick has been adopted for collecting the gases. The tube is about 5 feet in diameter, and extends about 5 feet into the throat of the furnace. It rests on six ribs of brickwork. In Langen's apparatus the gas collecting tube is placed externally to the furnace, which may therefore be kept filled with the charge. It consists of a bell-shaped tube, which rests on an inverted conical charging cup. The bell is suspended from a lever, and the charge is placed in the conical cup, so that when the bell is raised the materials glide into the furnace.

Twyers.—The twyers used for introducing the air into the blast furnace are subjected to intense heat, and require to be protected by a continuous circulation of water. They

are therefore made with a double casing of wrought iron,
cast iron, or bronze. Fig. 51 shows the arrangement of a
Staffordshire twyer. Another form, known as Lloyd's spray
twyer, is open at the back, and the cooling water, in the
form of spray, is driven from the end of a perforated pipe
against the port of the twyer. Another form, termed the
Scotch twyer (Fig. 52), consists of a spiral wrought-iron tube
enclosed in a cast-iron casing ; a current of water circulates
through the coil to keep it cool. The number of twyers
employed varies in different furnaces, according to the nature
of the fuel and the character of the ore. An excess of blast
causes the consumption of too much fuel, with the production
of white iron ; it also tends to cool the slags and impede the

Fig. 51.
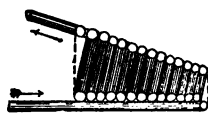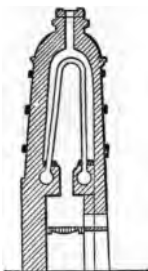
Fig. 52.   Fig. 53.

working. With an insufficient blast the temperature of the
furnace is lowered, and the production of iron lessened.
With small charcoal furnaces two or three twyers are used.
In large coke furnaces six or seven are arranged symmetri-
cally round the hearth, with their axes pointing a little away
from the centre. When producing forge pig the twyers are
arranged horizontally, or slightly inclined downwards, thus
causing a partial decarburisation. For foundry pig the
twyers are often slightly inclined upwards.

Hot-blast.—The use of hot air was first introduced by
Neilson at the Clyde Iron Works in 1828, and was soon
attended with great economy of fuel, and an increased
make of iron. The arrangements for heating the blast are
of two kinds—cast-iron pipes, through which air passes, and
heated externally ; and chambers of refractory brickwork,
constructed on the principles of Siemens' regenerators,
which are now in more general use.

Cast-iron Stoves.—Fig. 53 represents an old form of stove, which consists of a series of arched pipes of cast iron, arranged in an oblong fire-brick chamber ; along each of the long sides of this chamber are two circular mains, fitted with sockets, into which the legs of the vertical pipes are received, while between the mains, and running the full length of the stove, is a rectangular fire-place. The pipes are very unequally expanded by the heat, and this, when the extremities are fixed to the mains, leads to frequent breakages. The defects of this arrangement have caused many modifications to be introduced. Thus the horse-shoe pipes have been replaced by an inverted V shape, which gives a smaller radius of curvature to the arch; and greater uniformity of heating is obtained by introducing stops at intervals in the entry main, so that the air passes alternately backwards and forwards across the arch. In some works, the vertical pipes instead of being arched are united by short horizontal limbs at right angles, and are placed close together.
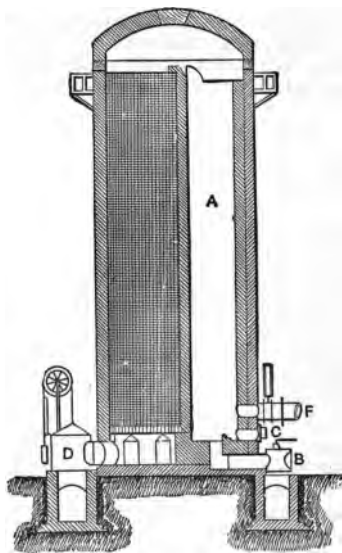
Fig. 54.

In many German works a number of horizontal pipes of elliptical section are arranged in a fire chamber, in a similar manner to the tubes in a locomotive, and united into a continuous serpentine coil by arched bends, which are external to the fire, thus lessening the tendency of these bends to break by irregular expansion.

Of the regenerative type, two principal forms are employed, invented respectively by Cowper and Whitwell.

Cowper's Stove (Fig. 54) is a circular wrought-iron tower, closed with a dome-shaped roof, and lined internally with fire-brick. It contains a circular fire-brick flame flue A,

into which the waste gases from the blast furnace pass by
the valve B. The body of the stove is occupied by checker-
work of fire-brick for absorbing the heat. The gas entering
the flue A, is there burnt, the air necessary for combustion
entering by the valve C. The hot products passing down
through the checker-work make it red-hot, and finally pass
into the chimney flue D.

The stove having been thus heated, the valves B, C, and
D are closed, and the cold-blast valve at the bottom of the
stove opened, together with the hot-blast valve F. The
cold air enters at the
bottom or cooler end,
and ascends through
the brickwork, getting
gradually hotter, and
then escapes by the
valve F, which com-
municates with the
blast furnace at a tem-
perature of 800° C.
Two stoves are worked
in conjunction, one
being heated by the
combustion of the
waste gases, while the
other is being utilised
in heating the blast.
These stoves are 50 to
55 feet high, and 20 to
25 feet in diameter.

Fig. 55.

Whitwell's Stove
(Fig. 55) differs from
Cowper's chiefly in the
arrangement of the absorbing brickwork. The air for
the combustion of the waste gases is admitted at several
points of the stove, so that the combustion is rendered more
perfect. The regenerative brickwork is built so as to form a
number of long and narrow vertical chambers, communicat-
ing with each other at the top and bottom. The blast
furnace gases enter through A, and meeting with warm air,
introduced through suitable passages, combustion takes place
and the flame rising up C, passes down the narrow passages,
etc., to the bottom. Here more air is admitted to burn com-
pletely the unconsumed gases, which rise up D and pass
down through another series of narrow channels, finally
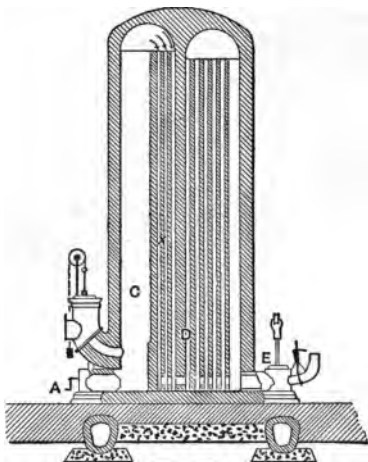
leaving at the chimney valve ᴇ. When the stove is sufficiently heated, which takes about two hours, the gas and chimney valves are closed and the blast valve opened, the blast entering in inverse order to the gases, as in the Cowper stove.

It is advisable to place the stoves as near to the furnace as is consistent with the other arrangements of the works, in order that the blast may retain as much of its heat as possible. With some charcoal furnaces the stoves are placed on a level with the furnace top, and the hot-blast main carried down vertically to the twyers; but much greater regularity of draught and freedom from dust is secured by bringing the waste gases to stoves on the ground level.
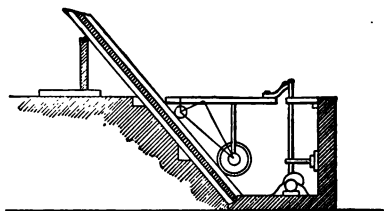
Fig. 56.

The advantages of hot blast are : (1) Economy of fuel, since less fuel is required, also the heated oxygen has a greater affinity for the carbon and hydrogen of the fuel ; (2) the blast penetrates the fuel more freely on account of its density being less ; (3) under equal circumstances, less pressure is required for hot than for cold blast ; (4) irregularities are better overcome with hot blast ; (5) it facilitates and accelerates the blowing in of a furnace. The disadvantages are :—(1) The pig iron is liable to be more impure, since silica, phosphoric acid, etc., are reduced to a greater extent, and (2) in consequence of the higher temperature the furnace walls are more quickly destroyed.

Lifts.—In hilly countries the blast furnace may be erected in a valley, the top being on a level with the ground. The charge is then tipped in without special apparatus. In most cases this is not possible, and lifts are required for raising the materials. These are of various kinds.

The inclined plane (Fig. 56) consists of a railway, between the ground and top of furnace, inclined at an angle of 30°. On this ncline runs a platform carriage, triangular in vertical section, with two pairs of unequal wheels. The power is supplied from a steam engine working a winding drum, around vhich passes a wire rope or flat-linked chain.

Colliery Lift.—This consists of a cage moving between vertical guides similar to those used in the shaft of a coal mine. It is worked by a direct-acting engine, fixed either on the ground or on the charging platform.

Water-balance.—This is a simple and effective lift still in use at several works, although more power is required for pumping water to the furnace top than for that of a direct lift; it is also difficult to keep the water boxes tight. It consists of two cages moving vertically between guides, and connected by a chain passing over a pulley. Below the floor of each cage is fixed a water-tight box provided with a discharge valve. When one cage is at the top, having discharged its load, water is caused to flow into its box until the weight is sufficient to pull up the cage which is loaded.

Pneumatic Lift.—This form of lift is now frequently used, the areas of the cylinders being adjusted for a pressure of from 4 to 7 lbs., so that the force of the air in the blast-main is sufficient to raise the required load. Gjer's lift (Fig. 57) consists of a large cast-iron ram, which works in a 36-inch cylinder, rising the whole height of the furnace. From this piston pass wire ropes over four pulleys down to

Fig. 57.

each corner of the lifting table, which is sufficiently large to hold four barrows. The weight of the ram is greater than that of the empty lift, and when the latter is at the top the ram will be at the bottom; so that by applying pressure beneath the ram, it rises, and the table is lowered. The loaded table is heavier than the ram, but when air is removed from under the ram a partial vacuum is formed, and the atmospheric pressure brings it down, and consequently lifts the loaded table up to the furnace throat.
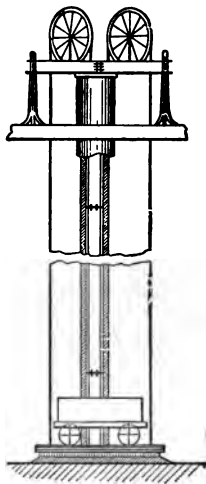
Blowing Cylinder.—This is used for supplying compressed air to the blast furnace. It resembles a steam cylinder, but is of larger dimensions, and the lateral openings for admission of air are often omitted. The piston is made of plates of cast iron fixed on an iron or steel shaft. On the circumference are arranged two leather rings which press against the sides of the cylinder, one for the up and the other for the down stroke. To avoid friction, fine plumbago dust is projected against the interior of the cylinder from time to time. Two sets of valves are arranged on the cylinder cover at each end ; the longer series open inwards for the admission of air as the piston recedes, and close at the return stroke ; then the other series or discharge valves open, and allow the compressed air to pass out.

Blowing cylinders do not furnish a regular supply of air, the air being compressed most at the middle of the stroke ; hence a "regulator" is placed in the course of the main between the engine room and the furnaces. The regulator is a cast-iron cylinder, open at the top and closed with a weighted piston. When the supply of blast is greater than is required, the piston rises ; but when the quantity diminishes, the piston falls, and exerts a compressing force until equilibrium is restored. If the blast main is of considerable length, or includes stoves, the regulator is unnecessary.

Blast Furnace Gases.—Owing to the larger consumption of fuel, coke furnaces give off more waste gases than charcoal furnaces. Kerl gives the composition of the gases as shown in the following table :

| | | Charcoal Furnaces. | | Coke F. | Coal |
		I.	II.	III.	IV.
Nitrogen,	etc.,	63·4	59·7	64·4	56·3
Carbonic oxide,	of	29·6	20·2	34·6	21·5
Carbon dioxide,	O_2	5·9	19·4	·9	15·2
Marsh gas,	CH_4	1·0	·3	—	4·2
Olefiant gas,	C_2H_4	—	—	—	1·8
Hydrogen,	H	·1	·4	·1	1·0
		100	100	100	100

The following table gives the composition of the gases from some British furnaces:

		Gartsherrie.	Alfreton.	Ormesby.
Nitrogen, . .	N	54·42	55·35	54·91
Carbonic oxide, .	CO	30·31	25·97	26·66
Carbon dioxide, .	CO_2	5·7	7·77	18·36
Marsh gas, . .	CH_4	3·45	3·75	—
Olefiant gas, .	C_2H_4	·14	·43	—
Hydrogen, . .	H	5·98	6·73	·07
		100	100	100

Scaffolding, Bears, etc.—Sometimes the charge of a furnace is obstructed in its descent ; the lower portion being melted and withdrawn leaves a " scaffold," which, with the increasing weight from above, often gives way suddenly, and falls into the hearth. This is called a " slip," and deranges the working of the furnace.

In some cases large ferruginous masses, called " bears," are formed in the hearth of a blast furnace, often containing iron, copper, silicon, graphite, manganese, nickel, cobalt, and cyano-nitride of titanium, a compound resembling copper in colour.

Desulphurisation of Iron.—Lime is capable of removing much of the sulphur from molten iron, and Saniter has shown that a mixture of calcium chloride and lime in the space of half an hour completely eliminates sulphur from molten iron. Calcium chloride is very cheap, being obtained as a by-product in the ammonia-soda process. Fluor spar in conjunction with lime has considerable desulphurising properties, but it exerts a destructive action on the basic linings of furnaces. In the Saniter process the mixture of lime and calcium chloride is put into the ladle, hot from a previous charge, and when molten cast iron is run in, the calcium compounds are melted, and rising upwards through the metal, remove the sulphur. Mr. Stead states : (1) that when sufficient lime is present in a furnace charge to combine with all the sulphur and silica (the temperature being sufficiently high) practically all the sulphur will be found in the slag and very little in the metal ; (2) that, if other things remain constant, as the temperature falls, so as to

produce pig iron of close texture, the sulphur increases, and when the temperature is just sufficient to melt the metal, most of the sulphur will be found in the iron ; (3) that the more basic the slag, the less sulphur will eventually be found in the iron ; (4) that if manganese is present, and the temperature sufficiently high, less sulphur will pass into the iron, and a greater amount will be found in the slag. This property is now taken advantage of in producing basic steel.* Massenez's process consists of mixing pig iron poor in manganese and high in sulphur with iron containing a larger percentage of manganese and but little sulphur ; the manganese of the one unites with the sulphur of the other, forming sulphide of manganese, which rises to the surface of the molten metal in virtue of its lower specific gravity. Ponsard mentions that 80 to 90 per cent. sulphur may be removed from pig iron by adding and stirring ferro-manganese in the ladle at the time of pouring. It is found that 2·6 parts of manganese remove 1 part of sulphur, the sulphur passing into the slag. Mr. Stead states that when manganese is combined with sulphur in pig iron, these elements do not prevent carbon assuming the graphitic condition as they do when in combination with the iron separately.

* See *Iron and Steel Institute Journal*, **II.**, 1892.

CHAPTER X.

REFINING PIG IRON.

Two distinct methods of refining pig iron have been adopted, depending on the kind of furnace employed, viz., the *hearth finery* and the *puddling furnace* methods. The chemical reactions are similar in both cases, being based on the oxidation of the impurities by oxygen, both in the gaseous and in the combined forms. The finery is now almost obsolete,
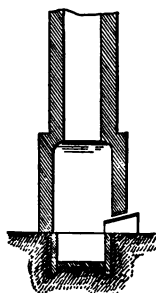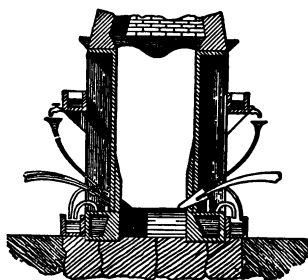
Fig. 58.   Fig. 59.

being only used for special varieties of iron in a few localities. It consists generally of a rectangular cast-iron hearth lined with charcoal, and the bottom is exposed to the air in order to keep it cool. Three sides are vertical, and the fourth slopes outwards. The flames escape into an open hood, or, as in Sweden, the hearth is covered with a cylindrical roof and communicates with the chimney by a lateral flue. The fuel is charcoal, and the blast is supplied through a single twyer. A view of the finery is given in Fig. 58. In South Wales

the pig iron was partly refined in a special hearth **termed**
the Refinery (Fig. 59), which consists of a cast-iron **frame-**
work having a refractory bottom. The front is closed **by a**
cast-iron plate, having a tap hole for the metal **and slag.**
The metal is run into a mould kept cool by water, **thus**
chilling the iron, making it white and brittle. As **white iron**
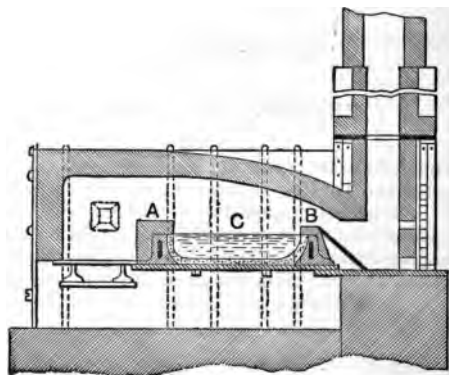
Fig. 60.
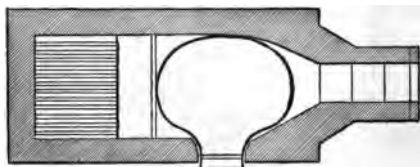
Fig. 61.

assumes a pasty state before melting, this property is useful
in iron required for treatment in the finery or for puddling
by the old dry method.

In 1784 Cort patented the puddling process, in which the
refining is carried on in a reverberatory furnace. He lined
the working bottom with sand, and employed white pig iron.
As the iron never became liquid, but only pasty, the name of
"puddling" was applied to it. This original process was

improved upon by Joseph Hall about 1820, who introduced the present method of pig boiling. In principle the operations are the same ; but in practice the chief difference lies in the construction of the furnace, the materials forming the furnace bottom, and the kind of iron employed. The furnace (Figs. 60 and 61) is a reverberatory, with a low, flat roof, generally sloping from fireplace to flue. The fire-bridge A and flue-bridge B are formed of hollow iron castings encased in brickwork. The bed is also formed of iron plates, and sometimes the sides consist of hollow castings kept cool by water or air. The laboratory or working part is about 6 feet long and 4 feet wide, tapering towards the flue-bridge. The grate area varies from one-third to one-half that of the laboratory. The bed is lined with broken slags,
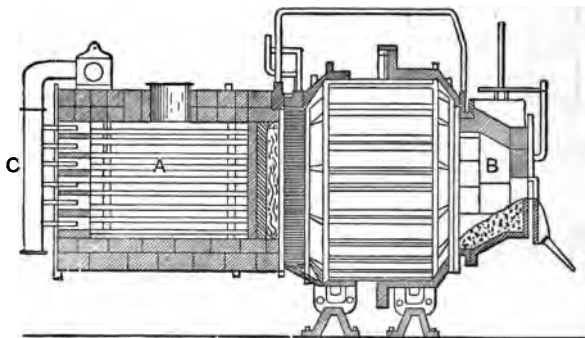
Fig. 62.

hammer-scale, and red oxide of iron, and the sides with bull-dog, all being well rammed down ; this is termed fettling.

Wet Puddling or Pig-boiling.—About 4 cwts. of grey pig iron are charged into the hot furnace, and gradually melted, which takes about 30 minutes. It is then rabbled for about 10 minutes, by which time the silicon and manganese are oxidised and formed into slag. A violent reaction now takes place, termed the boil ; this is due to the formation and liberation of carbonic oxide, which burns in jets at the surface. When this stage is over, granules of metallic iron separate, and the whole becomes pasty ; this is termed " coming to nature." The phosphorus is also oxidised and

most of it passes into the slag during this stage. The metal
is then collected into balls of about 90 lbs. each, which are
next taken to the hammer and rolls. A little manganese is
very beneficial in refining iron. It retards decarburisation,
it takes up oxygen from the iron, thus reducing it and
saving the iron from passing into the slag, and the presence
of manganese as oxide in the slag makes the slag more
fluid, and is thus more easily expelled from the iron in
shingling and re-heating. The slag is therefore a silicate
of iron containing manganese, phosphorus, and other im-
purities previously present in the pig iron.

Mechanical Puddling Furnaces have been introduced
from time to time, but with only a very moderate degree of
success. One of the best is that of Danks (Fig. 62). It
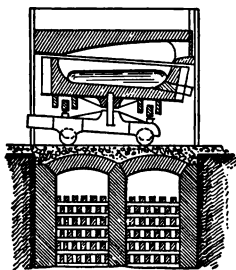
consists of a cast-iron cylinder with
conical ends, 4 feet long, 5½ feet
in greatest diameter, bound with
iron hoops. The cylinder is en-
circled with a roller-way, which
rests on anti-friction rollers. One
end is open to the fireplace, and
the other opens into the elbow-
shaped movable flue B, at which
end the charge is withdrawn. The
fireplace has an air-blast o, placed
below the grate, and small twyers
are also placed in the back wall
through which air is blown at the
level of the fire-bridge. The fur-
nace is lined with oxide of iron in
which lumps of a hard kind of ore (ilmenite) are embedded.
When the charge is introduced along with 20 per cent. of
slag into the hot furnace, the furnace is caused slowly to
rotate, and the speed increases as the operation proceeds.
The action is the same as in the ordinary puddling furnace,
and the iron is collected into one large ball of about
700 lbs.

Fig. 63.

Pernot's Furnace (Fig. 63).—This was introduced some
years ago at St. Chamond, France. It consists of a fixed
roof and circular turning bed, inclined at an angle of 6°.
Both ordinary fuel and gaseous fuel have been used. The
bed is made of hollow wrought-iron segments, and fettled in
the usual way with iron oxide and cinder (slag). It is sup-
ported on an iron carriage which has two pairs of wheels, and
upon the framework is mounted the socket of the revolving

axle of the bed. Rotation is imparted by means of an endless screw and worm wheel. The charge consists of 20 cwts. of pig iron with some scrap iron. The action is the same as described for ordinary puddling. The inclination of the bed causes the lining to be alternately under the molten iron and exposed to the flame, so that the bottom heat is constantly renewed and sticking of the charge prevented. This action favours alternate oxidation of FeO, and reduction of the Fe_3O_4 by the carbon present. The rotation of the furnace replaces manual rabbling and promotes the reaction of the lining on the pig iron. The bed being removable, all parts can be made easily accessible for repairs.

Gas Furnaces for Puddling.—By the use of gas producers, fuel may be used which is much too inferior for ordinary furnaces, and a higher temperature obtained by the combustion of the gas formed than by using solid fuel directly. The puddling operation is the same as usual, except in such arrangements as Pernot's, where gas may be used in combination with mechanical puddling. In the case of Siemens' furnace (see Figs. 82A and 83), the regenerators are liable to be choked with dust, slag, and iron, carried over during the boiling stage. This may be largely remedied by passing the waste gases through an intermediate chamber, so as to deposit the solid matter before entering the regenerators. In some cases certain ferruginous substances have been placed at the entrance of the regenerators to act as a kind of filter. The difficulties arising from the deposition of dust, etc., have prevented the use of gas in many forges. The extreme heat produced in Siemens' furnace probably increases the affinity of iron for carbon, which renders the fining difficult, and tends to produce an imperfect, steely iron.

Waste Heat.—The waste heat of furnaces used for refining iron has been utilised in a variety of ways, but chiefly for heating steam boilers. The commonest form of boiler is a vertical cylinder with hemispherical dome, placed in the chimney. The flame passes round it, or through a central flue connected with the outer shell by horizontal tubes. Two furnaces are generally connected with one boiler.

The loss in puddling varies, according to the impurity of the pig iron employed, from 5 to 10 per cent. ; and the fuel consumed is from 20 to 25 cwts. per ton of iron bars produced. The charge of pig iron is 4 to $4\frac{1}{2}$ cwts. for an ordinary furnace, and in Staffordshire five to seven heats are worked off in twelve hours.

Treatment of Puddled Iron.—The spongy mass of iron from the puddling furnace is conveyed direct to a hammer or squeezer, in order to consolidate the metal and expel the mechanically enclosed slag. The *helve hammer* consists of a heavy mass of cast iron weighing from 2

Fig. 64.

to 10 tons, and is lifted by projecting pieces fixed in a cam
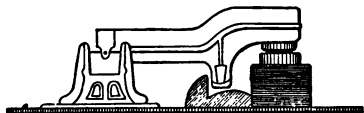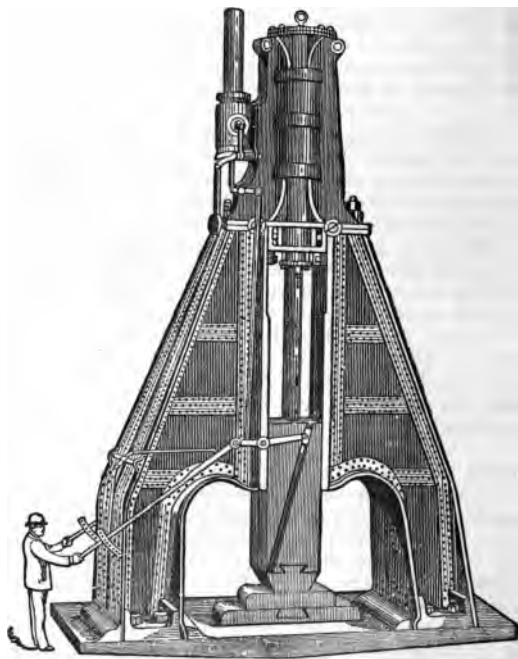
Fig. 65.

ring ; it falls by its own weight through a space varying from 16 to 48 inches. Fig. 64 represents a belly-helve in

which the cam is placed below the surface of the ground, and acts on the projecting part of the hammer.

The *steam hammer* (Fig. 65) is now largely used for shingling and welding It is a simple, direct-acting machine, and takes up little room compared with the cumbrous wheel-work of the old helve. The force of the blow in shingling is generally required to be light at first, and with the steam hammer the force can be varied with the work to be done. Another advantage is, that the hammer always works parallel with the piece under operation, which is not the case with helves, the hammer-man having to use thickness pieces to overcome this difficulty. Both sides of the steam hammer are also accessible for working. It consists essentially of a vertical high-pressure engine with an inverted cylinder. The piston-rod is attached to a heavy block or " tup " moving between guides on the inner faces of the standards, which
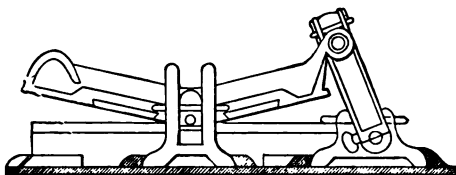
Fig. 66.

consist of a massive cast-iron framing. The ordinary hammer is double-acting, the steam being exhausted above and below the piston. The hammer varies in weight from 30 to 60 cwts., but the force of the blow is, to a great extent, independent of the mass of the hammer head.

Squeezers are of two kinds—lever and rotatory. The *crocodile squeezer* (Fig. 66) is made with both single and double jaws. The lower jaw is fixed while the upper one is opened and closed by a crank and connecting rod attached to one end. The upper jaw is sometimes serrated so as to better grip the puddled ball, which is inserted at the wide end and gradually rolled by the workman towards the middle. A *rotatory squeezer* is represented in Fig. 67, which consists of a revolving cylinder (*a*) having its surface studded with teeth. This cylinder is placed eccentrically with regard to that of the outer casing (*b*). The ball is placed in the space (*c*) and carried forward by the rotation of *a*, thus being gradually consolidated and the slag squeezed out.

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Mr. Danks devised the one shown in Fig. 68. *a, a* are two roughened parallel rolls, 4 feet long and 18 inches in diameter, both revolving in the same direction, and above these, on a parallel shaft, is a large cam, the periphery of which
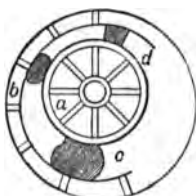
Fig. 67.
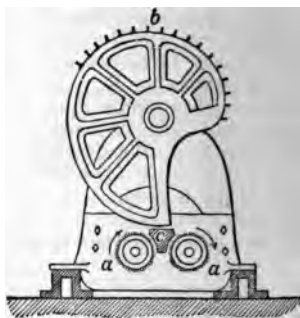
Fig 68.

revolves at the same rate as the surface of the two rolls. At the end of the rolls is fixed a horizontal steam hammer (*c*) which hammers the bloom while it is being squeezed by the cam and rolls.
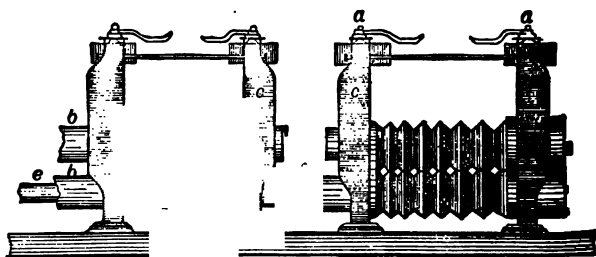
Fig. 69.

Rolling Mill.—The forge train (Fig. 69) contains two sets of rolls—the roughing rolls (*a, a*), about 5 feet long and about 20 inches in diameter, containing a series of Gothic and diamond-shaped grooves which are roughened so as to grip the iron ; and the finishing rolls, with rectangular channels,

which diminish in size from right to left. The roughing rolls revolve at about 70 revolutions per minute, and the finishing rolls at about 90 revolutions per minute. The iron is first passed through the largest groove, and so on to the smallest, or until the bar is of the desired thickness.

Re-heating and Welding.—The bars and slabs of iron obtained by shingling and rolling puddled bars, require to be refined if the best malleable iron is desired. They are cut up into short lengths, arranged in faggots or bundles, then re-heated and welded by hammering and rolling. These piles are about 2 feet long and 4 inches square for ordinary bars, and 5 to 6 feet long and 12 inches square for large sizes. Each bundle is bound together with iron wire. For iron plates, bar iron is piled in suitable lengths, and for large sheets each pile weighs about 70 lbs. The ordinary re-heating furnace (Fig. 70) is somewhat similar in shape to the
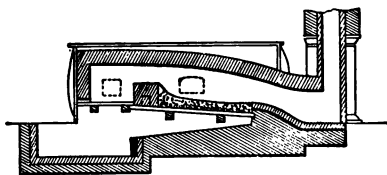
Fig. 70.

puddling furnace; the bed is flat and slightly inclines towards the flue and is lined with sand. It is essential that the fireplace should be large enough for the furnace to be rapidly raised to a white heat; the ratio of the section of the fireplace to the bed being about 1 : 2. The slag runs off the bed to the bottom of the flue and is termed "flue cinder." The impurities which have not been eliminated in the previous operations are largely removed in re-heating and welding. The enclosed slag liquates out as a fluid basic silicate, leaving a black residue mixed with magnetic oxide, Fe_3O_4, which is removed in hammering and rolling. This basic slag acts on the manganese, silicon, phosphorus, etc., oxidising them, and the oxides pass into the slag.

Furnaces using gaseous fuel have been largely used for re-heating, such as that of Ponsard (Fig. 71). In this arrangement the gas from the producer is delivered directly to the furnace and burnt with hot air which is heated by a "recuperator" placed beneath the surface. The recuperator

is a brick chamber, partly solid and partly hollow, contain-
ing a number of vertical passages, the adjacent ones being
separated and the alternate ones connected by horizontal
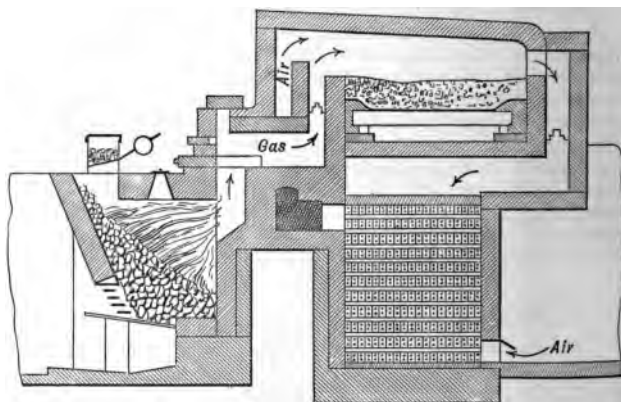
Fig. 71.

passages in the perforated bricks. The flame passes down-
wards, while the cold air, admitted at the bottom, passes
upwards by separate channels. The action is continuous.
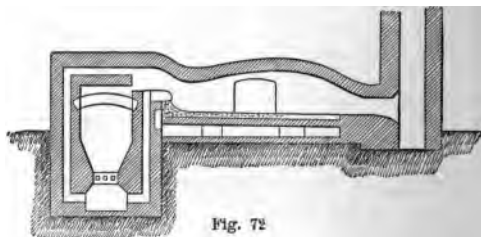
Fig. 72

The Boëtius furnace differs from the preceding one in the
manner of heating the air required for the combustion of the
gas used. Fig. 72 shows the general arrangement in vertical
section. The gas producer is constructed with passages in

its walls, through which the air supplied to the furnace is compelled to pass, thus being heated. It meets and mingles with the gas at the furnace bridge, where combustion takes place.

The Bicheroux furnace is used both for puddling and re-heating with gaseous fuel. The gas is made in an ordinary Siemens' producer built with the furnace, and burned directly, as in the Ponsard and Boëtius methods. The air for combustion is heated by contact with the bed of the furnace, a broad flat flue which runs under the bed being provided for this purpose. It is also further heated by circulating round a large vertical pipe which conveys the gas from the producer to the furnace. In a modification of this furnace, termed the Casson-Bicheroux, the walls of the producer are made with narrow channels, as in the Boëtius plan, in order to provide an additional supply of hot air.

COMPOSITION OF REFINING SLAGS.

	From a refinery	From a puddling furnace.	From a re-heating furnace.
Ferric oxide (Fe_2O_3), . .	—	8·27	—
Ferrous oxide (FeO), . .	65·52	66·32	76·73
Silica (SiO_2), . . .	25·77	7·71	15·15
Manganous oxide (MnO), .	1·57	1·29	1·51
Alumina (Al_2O_3), . .	3·60	1·63	1·95
Lime (CaO), . . .	·45	3·91	—
Magnesia (MgO), . . .	1·28	·34	—
Sulphur (S), . . .	·23	1·78	1·36
Phosphorus (P), . .	1·37	—	—
Phosphoric acid (P_2O_5), .	—	8·07	2·22
	99·79	99·32	98·92

TINNING IRON PLATES.

The plates are first thoroughly cleansed in warm dilute sulphuric acid, then washed and scrubbed with sand to remove all traces of rust, which would prevent the tin from adhering ; the plates are then immersed in a bath of melted tallow, which dries them thoroughly. The tinning arrangement comprises six pots, each heated by a separate fire and

termed respectively—the tinman's pot, tin pot, washing pot (divided into two compartments), grease pot, cold pot, and the list pot. The plates from the tallow or tinman's pot are placed in the tin pot, the surface of the molten tin being covered with tallow to prevent oxidation ; after being heated for an hour and a half in the melted metal they are removed, drained, and plunged into the first division of the washing pot, which also contains molten tin ; then removed and brushed to remove excess of tin ; afterwards they are quickly dipped in the tin in the second division to remove the brush marks. They are then transferred to the grease pot containing melted tallow, which removes any excess of tin by draining. After about ten minutes the plates are inserted in melted tallow contained in the cold pot. Lastly, in order to remove the tin which has drained down and formed a bead at the lower edge of the plate, the edge of each plate is dipped in the list pot, which contains melted tin about ½ inch deep ; then by striking the plate sharply with a stick the superfluous metal is detached. The plates are rubbed with bran, and afterwards with sheepskin, when they are ready for use.

An inferior variety of tin-plate, in which the iron is coated with an alloy of tin and lead, is termed "terne plate."

GALVANIZING.

Galvanized iron is a term applied to iron plate and iron articles coated with zinc, to prevent the iron rusting. The zinc was originally deposited by means of an electric current. It is now manufactured by dipping the clean iron into a bath of molten zinc, the surface of which is covered with sal-ammoniac in order to prevent oxidation, and at the same time to remove any oxide that may be formed. The iron is cleansed in dilute sulphuric acid before dipping it in the molten zinc.

CHAPTER XI.

STEEL.

NATURE AND PROPERTIES OF STEEL.

STEEL is a compound of pure iron with carbon in sufficient quantity to enable it to be made sensibly harder when raised to a red heat and plunged into water. The quantity of carbon necessary to produce this effect is about ·25 per cent., but the metal is capable of being thus hardened to a greater degree in proportion to the quantity of carbon present, which in steel may be increased to nearly 2 per cent. The term steel is also applied to iron containing less than ·25 per cent. carbon if the metal has been melted and poured into a mould ; but it would be much better to term it ingot iron, and limit the use of the word "steel" to those compounds of iron which are capable of being hardened and tempered. When another element besides carbon is added to iron, the metal is named after the added element : thus we have manganese steel, chrome steel, tungsten steel, etc. The term "mild" is applied to steel and ingot iron which contains less than about ·3 per cent. carbon. Howe considers steel to consist of a matrix of comparatively pure iron in which are embedded crystallised bodies also containing iron, and by their properties affect the mechanical properties of the whole mass, although less than do changes of corresponding magnitude in the composition of the matrix.

Properties.—Steel, in the soft state, has a white colour with a bluish tinge, and becomes whiter when hardened, sometimes almost pure white. The lustre is similar to that of iron. When freshly broken the fractured surface affords some indication of its quality, being generally finely granular or crystalline, uniform in structure and destitute of fibre ; but these will vary with the mode of breaking, and with the amount of carbon and other elements which the steel con-

tains.   Much carbon makes steel close-grained and lustrous.
When mild steel is broken by a sudden blow the surface is
crystalline ; but when broken with progressive stresses, the
appearance inclines to the fibrous state.   The tenacity of
good steel is very high, exceeding that of any other metal,
and is increased by cold-rolling, or by wire-drawing.   Steel
possesses the valuable property of being hardened by quick
cooling after heating, and hard steel may be annealed or
softened by making it red-hot and cooling it slowly.   The
hardness of hardened steel may be reduced by gradually rais-
ing it in temperature up to a certain point, when it becomes
highly elastic ; this operation is termed "tempering."   Steel
requires to be welded at a lower temperature than iron, and
its power of being welded diminishes with the increase of
carbon.   The melting point of steel is probably from 1400° to
1500° C., the fusibility increasing with the amount of carbon
and other elements present.   The specific gravity of steel
varies from 7·6 to 7·8, being slightly less in the hardened
than in the softened state, in consequence of the increase in
bulk caused by this process.   Steel resists the influence of
magnetism more than iron, but when magnetised the
property is permanent ; the presence of much manganese
prevents the acceptance of magnetic power.   Steel is less
readily oxidised by exposure to air than iron ; but the pre-
sence of other metals, such as manganese and chromium,
increases its liability to oxidation.

Phosphorus is much more hurtful to steel than to iron,
and the more phosphorus a steel contains the more readily
does it lose its characteristic properties by repeated heatings,
becoming finally incapable of being tempered.   Phosphorus
hardens steel, increases its tensile strength, makes it cold-
short, more fusible, brittle, more rigid and less elastic,
especially when the carbon is high ; it also lowers the
melting point, and induces a coarse crystalline structure.

Silicon is capable of combining with iron to the extent
of 30 per cent.   Good steels have been made with ·5 and
even up to 2 per cent. silicon.   It hardens steel less than
phosphorus does.   It injures high carbon steel more than
mild steel, and tends to make the steel red-short, which
may be counteracted by the presence of manganese.   Silicon
readily unites with oxygen to form silica SiO_2, and as this
compound has a strong affinity for bases, it passes into the
slag.   Silicon diminishes the power of iron to combine with
carbon.

Sulphur is generally injurious to steel, making it red-

short, more fusible, brittle, and less tenacious. It hinders steel from welding, but is not so injurious in cold working. Manganese neutralises the bad effects of sulphur.

Carbon.—This element probably exists in steel in two forms, corresponding somewhat to its condition in cast iron. (1) As hardening carbon, when it is wholly combined with the iron, or in solution in the iron. (2) As cement carbon, when it is present as a free carbide, to which the formula Fe_3C is assigned. This is the condition of the carbon when the steel is soft. When other elements are also present, such as silicon, manganese, phosphorus, or sulphur, they probably modify the power of carbon to pass into the above different states. The alteration in the condition of the carbon is brought about by different heat treatment; thus in Fig. 73, at temperatures above w, the carbon is wholly in the hardening
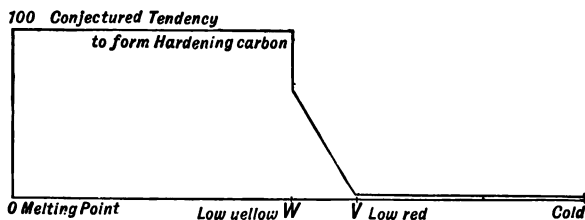
Fig. 73.

form; below v it is wholly in the cement or carbide form; while between w and v the condition of the carbon is partly in one form and partly in the other. If a piece of steel with sufficient carbon is rapidly cooled from a temperature at or above w, it will be hard; if it is rapidly or slowly cooled from below v, it will be soft. At temperatures between w and v, the carbon in a mass of gradually cooling steel passes from the condition of hardening carbon to that of cement carbon and *vice versa*.

Hardening.—Steel with upwards of ·3 per cent. carbon is made very hard by raising its temperature to a red heat and plunging it in some liquid capable of rapidly cooling it; and the hardness, when cooled from a certain temperature, will be in proportion to the rapidity of cooling. Take three liquids of different conducting powers for heat—mercury, water, and oil—and raise the pieces of steel to the same temperature, then plunge one into each of the above liquids,

when it will be found that mercury gives the greatest degree
of hardness and oil the least. If any substance is added to
water, such as an acid, so that its conductivity is increased,
then its hardening power will also be increased; or, if the
water be heated, so that it cools the steel less rapidly, the
hardening power is diminished. The temperature to which
it is necessary to heat the steel before quenching has been
already explained. The effect of hardening is to increase the
hardness, raise the elastic limit, increase the tenacity (if the
cooling has not been too sudden), and diminish the ductility.
In most cases oil hardening gives the highest tensile strength.
A moderate temperature before quenching is best, and the
higher the content of carbon the lower the temperature
required. The hardness and brittleness of steel are in-
fluenced more by cooling from a cherry-red heat to 300° or
400° than from those temperatures downwards. With large
castings and forgings containing less than ·75 per cent. of
carbon, the tensile strength is more important than the
hardness; hence they are hardened in oil. In cutting and
similar tools hardness is the chief requisite ; therefore they
are hardened in water.

Cause of Hardening.—The general explanation is that
the sudden cooling preserves the condition of the steel which
existed at a red heat, e.g. the mode of existence of the
molecules of both carbon and iron. Another explanation
states that hardness is due to unequal stresses set up by
cooling the outer layers of the metal much quicker than the
interior, and by the compression of the exterior the super-
ficial density and hardness is increased. Now, by annealing,
which is the reverse of hardening, the metal is caused to flow
and the tension is relieved. If the hardened metal is heated
to 250°, the particles are rendered sufficiently mobile to
relieve a part of the strain, and the steel is said to be
tempered. Abel has shown that at a straw heat (230° C.) the
condition of the carbon changes. Akerman considers that
hardening is due to the compression, caused by sudden cooling,
forcing the carbon into the hardening state. Osmond has
introduced what is known as the "allotropic theory." If a
bar of unhardened steel be heated to 500° C. and allowed
slowly to cool, no break in the uniformity of the cooling
occurs ; but if the steel be heated to 900°, or even 700°, there
are stages where the cooling is interrupted. This is probably
due to some molecular change in the steel, which produces or
absorbs heat. Like irregularities occur during gradual heat-
ing. These effects may be observed with great accuracy by

the aid of the Le Chatelier pyrometer.* Thus in Fig. 74 the curves of pure iron, mild steel, and hard steel, respectively, are obtained by observing the motion of the spot of light reflected from the mirror of the galvanometer, when the thermo-couple is attached to the cooling metal. Suppose the metal to cool uniformly at the rate of 2·2° per second, then at 858° C. there is a retardation of the motion of the spot, and what took 6·6 seconds here takes 26 seconds in the case of pure iron, and a similar retardation of 76 seconds in the case of hard steel. With respect to mild steel there are
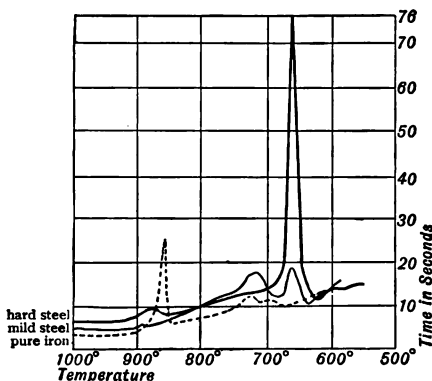
Fig. 74.

two breaks in the continuity of the cooling, one above and one below 700°. Now Osmond observed that the effects of cold working and quenching from a high temperature on steel were very similar, and concluded that they must arise from a common cause. He supposes that the condition of the carbon is probably not changed by cold working, and therefore the hardening effect is due to an allotropic change in the iron itself. He considers that iron assumes two allotropic forms, viz., (a) iron which exists in soft iron and steel, and is itself soft and malleable ; (β) iron which is hard, strong, and brittle, and which exists in hardened steel. He states that one variety changes to the other variety at certain critical temperatures. If carbon and other bodies are absent, these

* See Fig. 20, p. 95.

changes occur rapidly, and however quickly pure iron is quenched from a high temperature, the (β) is entirely changed to the (a) form.   But if carbon is present it impedes this passage of one kind to the other, and if the steel be suddenly cooled the iron remains in the (β) form, and is therefore hard. In cold working the (a) is also changed into the (β) form.   In the curve (Fig. 74), it will be observed there are two irregularities in the cooling of mild steel: the first is assumed to be due to the $a - \beta$ change, but the second is due to the passage of hardening into cement carbon.   This point was first observed by Gore and afterwards by Barrett, who gave the name of recalescence to the phenomenon of re-heating exhibited by iron when cooled to a certain point.   Osmond reasoned that if steel be quenched below the temperature represented by the first break, but above the temperature at which the carbon change occurs, then the steel should be soft and yet the carbon not in the cement form, and such he affirms to be the case.   But Arnold and others have failed to verify this result, and affirm that the hardness change is coincident with the carbon change.   Professor Arnold says: "Whether the hardness of quenched high carbon steel is due to the individual properties of an extremely attenuated carbide of iron, or to an allotropic change produced in the iron itself by the presence of dissolved carbon, there is no evidence to show."

Mr. H. M. Howe says, "There are two prominent theories of hardening, and both hold that sudden cooling acts by retaining a special condition which is reached at a red heat, but which would be departed from in slow cooling.   On the carbon theory it is a special known hardening condition of carbon ; on the allotropic theory, it is a suspected hard, strong, brittle 'beta' modification of the iron that causes hardening, and that the carbon simply acts in retarding the change from hard 'beta' to soft 'alpha' iron.   With the allotropic theory is associated the belief that the distortion in cold working also induces the 'beta' modification, or another modification which has been termed 'delta' iron." Howe considers that the effects produced by cold working in modifying various qualities of the metal are too great to be referred to mechanical action, hence they must be due to some chemical or physical cause.   The chemical condition of carbon does not change, hence the iron must change allotropically.   He also thinks that other metals undergo a similar allotropic change.   One strong argument in favour of allotropy is the sudden disappearance of magnetic pro-

perties in heating, the sudden change of specific heat and the spontaneous retardations which occur in cooling practically carbonless iron, which, when sufficiently rapidly cooled, also has its tenacity nearly tripled. The effects of cold working and sudden quenching are identical in raising the elastic limit, tenacity, hardness, and brittleness, and in lowering the density. But the difference between the hardness, brittleness, and conductivity is enormous, and gives rise to the question as to whether "delta" and "beta" iron are identical. With respect to the action of carbon, Howe suggests that hardening is not due to "beta" iron alone, carbon only acting as a heater, but to a combination of "beta" iron with carbon. He calls this the "carbo-allotropic" theory. From the non-magnetism of "beta" iron and of manganese steel, the latter is supposed to contain "beta" iron. The great tensile strength of quenched carbonless iron is also assumed to be due to "beta" iron, but in this case there are absence of glass-like hardness and brittleness, therefore "beta" iron may be assumed to be a strong ductile and moderately hard substance, and "beta" carbide exceedingly hard and brittle. The carbo-allotropic theory may be formulated thus. Hardening is due chiefly to the preservation, by sudden cooling, of a hardening carbide of "beta" iron of perhaps varying composition, and often, especially in low carbon steel, to "beta" iron alone, but the hardening carbide gives much the greater hardness and brittleness ; and, secondarily, to intense residual stress.[*]

Tempering.—By cautiously re-heating hardened steel to a certain point, the tension is greatly released, some carbon or carbide is set free, and the metal loses its brittleness, and becomes softer in proportion to the temperature to which it is raised ; so that by this means various degrees of hardness may be produced in the same steel to suit the requirements of different articles. This operation is termed "tempering." The surface of the steel is made bright before heating, and when the temperature reaches 220° C. a faint yellow colour appears, succeeded by other colours as the temperature rises, so that the colour indicates the temperature of the steel, and therefore the degree of softness or "temper." These colours are due to a thin coating of oxide, which forms on the surface and produces the colour as an optical effect. The following table shows the tempers used for various articles, the lowest temperature indicating the hardest temper :

[*] Iron and Steel Institute Meeting, 1895.

Temperature.	Colour.	Article.
220° C.	Faint yellow.	Surgical knives.
230	Straw yellow.	Razors.
255	Brownish yellow.	Scissors, hard chisels.
265	Purplish brown.	Axes, planes.
277	Purple.	Table knives.
288	Light blue.	Swords, springs.
293	Dark blue.	Fine saws, augers.
316	Blackish blue.	Hand saws.

When the steel is heated much beyond this point (316° C.) it becomes too soft for any kind of tools. The term "temper" is used to express the hardness, whether due to treatment or composition.

All kinds of steel expand on hardening, varying with the amount of carbon present. The temperature to which steel should be raised for purposes of hardening must be regulated according to the quantity of carbon it contains, since overheating is highly injurious. The harder the brand of steel, that is, the more highly carburised it is, the lower will be the temperature required ; moreover a small article will require a lower temperature than a large one made of the same steel, because it is more suddenly cooled. Bulky articles, such as the face of an anvil, cannot be hardened by plunging into water face downwards, but must be placed upright in water and deluged with a large stream of cold water falling from above. The same remarks also apply generally to smaller articles having steel faces.

Welding Steel.—It is much more difficult to weld steel than iron, and the greater the amount of carbon the greater is the difficulty. Various fluxes have been recommended to prevent the carbon burning away, and to render the welding surfaces clean, but few of them have come into common use; sand, and a mixture of borax and sal-ammoniac being the best. It is important that the temperature of the metal should not be raised higher than absolutely necessary ; the higher the amount of carbon the lower should be the temperature used, hence the necessity of heavier hammers. The pieces should be tapped gently at first, and when they have begun to adhere they may be struck more heavily. The temperature at the finish must not be too low. It is best to work the steel rapidly, re-heating as often as necessary (in order to prevent finishing too cold), and to anneal the whole piece when finished, so as to correct the effects of local hardening. When steel is to be welded to iron, the latter may be at a higher temperature than the former with advantage.

METHODS OF PRODUCING STEEL.

The different methods of making steel may be classified thus :—(1) By direct methods, as in the Catalan forge, etc. ; (2) from pig iron in the finery; (3) by puddling pig iron; (4) by the cementation process ; (5) by the treatment of blister-steel, or iron and carbon in crucibles ; (6) by a pneumatic process, such as that of Bessemer ; (7) in an open hearth such as that of Siemens.

1. **The direct methods** in the Catalan forge, Siemens' rotator, Blair's furnace, etc., have been described when treating of iron.

2. **Finery method.**—This differs but little from that employed in making iron, the operation being conducted so as to leave sufficient carbon in the bloom to constitute steel. This is done by prolonging the operation, thus leaving the iron a longer time in contact with incandescent carbon, and by using a less oxidising blast. The best pig irons for this purpose are the strongly-mottled and spiegel-eisen varieties. This method is now almost obsolete.

3. **Puddling method.**—This is essentially the same as that used for wrought iron, but greater care is required in selecting the pig iron employed, which should preferably contain manganese. This metal acts in retarding the decarburisation, in consequence of its superior affinity for oxygen, by constantly reducing tetroxide of iron to protoxide, and the protoxide to metallic iron, thus preventing the carbon from being oxidised. Oxide of manganese also produces a very fluid slag, which is easily expelled. A little metallic manganese improves the quality of steel. The addition of spiegel-eisen to the charge of non-manganiferous pig iron does not answer so well as when the manganese already exists in the pig iron employed.

A thinly liquid slag protects the iron from a too rapid oxidation, and thus permits a more prolonged rabbling, so as to remove the impurities other than carbon. A slag with a double base of FeO and MnO, containing about 10 per cent. of the latter is very fusible, and but feebly decarburising. Only one class of iron is operated upon at a time, as in a charge of mixed irons one kind would be purified sooner than another.

The melting of the charge must be rapidly performed in order to lessen oxidation. The rabbling requires great care, and when the metal " comes to nature " in the form of fine

white, brilliant grains, it indicates good and uniform steel. A lower temperature is employed during the final stages of the rabbling period than when puddling for iron, so that the metal separates more readily while carbon is still present in it.   The balling is done in a neutral atmosphere, and the balls taken quickly to the hammer.   Eight to nine charges of iron would be worked off in the same time as six to seven of steel.

4. **Cementation Process.**—This consists of exposing bars of malleable iron in contact with charcoal to a high and prolonged temperature, in closed vessels from which the air is excluded, in this way forming blister steel.   The furnace (Fig. 75) is rectangular in plan, and covered with an arch having a hole 12 inches square in the centre, which hole is opened during cooling.   It contains two rectangular firebrick or fire-stone vessels, arranged one on each side the fireplace, which runs the whole length of the furnace.   Each of these vessels is about 12 feet long and 4 feet square, but the sizes differ in different works.   Swedish bar iron is preferred for making the best kinds of steel, and hammered bars are generally preferred to rolled bars.   Ordinary sizes of bars for cementation are 2 to 5 inches wide and $\frac{3}{4}$ inch thick.   The pots are charged by covering the bottom with coarse charcoal, and on this is placed a row of iron bars about half an inch apart, and so on alternately until the vessel is full.   The top is then covered with wheel-swarf or mud from grindstones, which melts and forms a glaze when heated, thus excluding the air.   The charge for one pot may be from 15 to 30 tons of iron.   Two small holes are left in the furnace, corresponding to two similar holes in the vessels, through which a bar, termed the "trial bar" or "tap bar," projects from each vessel.   When the fire is lighted, two or three days are required to obtain the proper temperature, which is then maintained from seven to nine days, according to the temper of steel required, the hardest steel requiring the longest time.   On examining the trial bar from time to time by withdrawal and fracture, the conversion is seen to have penetrated gradually to the centre : the vessels are then allowed six days to cool down.   Conversion begins at a temperature of 1000° C., but goes on more actively at 1170° ;

Fig. 75.

at higher temperatures cast iron is produced. By cementation the fibrous iron is changed to a more or less crystalline steel, and the surface of each bar is covered with blisters, which in good steel are small and fairly regular. These blisters are probably due to the reduction of oxide of iron contained in the enclosed slag and the evolution of carbonic oxide. The fractured surface shows a reddish-white, crystalline structure, which is darker in colour and finer in grain the greater the amount of carbon. If air has gained access to the bars during conversion, they are rough on the surface and have a skin of iron. When the temperature has been too high, and fusion on the surface has taken place, they are called "glazed" bars. Both aired and glazed bars are unfit for making best cast steel.

The manner in which the carbon passes through the iron so as to produce cement steel is unknown : it may be transmitted in the form of gaseous compounds of carbon, such as carbonic oxide CO, cyanogen CN, and hydrocarbons, such as marsh gas, CH_4. According to this view the gases are decomposed in the pores of the bars, and the carbon unites with the iron. The CO gives up carbon, being changed to CO_2, thus :

$$2CO = CO_2 + C.$$
Carbonic oxide. Carbon dioxide. Carbon.

The nascent nitrogen and hydrogen, liberated from the cyanogen and marsh gas, on passing outwards, are brought in contact with charcoal, with which they again unite. Also carbon dioxide takes up fresh carbon, forming carbonic oxide, thus :

$$CO_2 + C = 2CO.$$
Carbon dioxide. Carbon. Carbonic oxide.

These gases act as vehicles for the transmission of carbon to the interior. On the other hand, it may be that the gaseous compounds of carbon are decomposed at the surface of the bars, and the combined carbon transmitted to the interior. We may assume that solid carbon unites directly with iron, on the surface of the bars with which it is in contact.

Blister steel is used for common purposes without further treatment, but generally the bars are fagoted and welded one or more times. Re-heating tends to decarburise the steel, so that the surfaces of the piles are covered with clay, or with sand and borax, which forms a fused coating and protects the metal from oxidation. "Spring steel" is obtained by re-heating and drawing out between rolls the variety

of cement steel termed "spring heat." "Shear steel" is obtained from a better quality first drawn out into bars, then fagoted and re-heated. "Double shear steel" is of still superior quality, generally re-heated and welded, then again cut up, heated, and welded.

The texture of blister steel is modified according as it has been rolled or hammered. Hammered steel has a finer grain and a more compact structure than rolled steel; it has a greater power of resistance, with greater uniformity and density.

Case-hardening.—This is a kind of cementation on a small scale, and consists of the production of a surface coating of steel on iron articles, by exposing them to a high temperature for a short period, in contact with carbonaceous matter.   The articles are enclosed in an iron case with charcoal, leather, ferrocyanide of potassium, K_4FeCy_6, etc., and
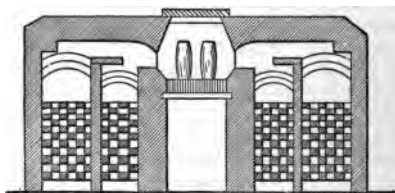
Fig. 76.

the case made air-tight; then the whole is heated in a furnace for a time proportionate to the thickness of the steel facing required.   The conversion may extend to a depth of $\frac{1}{4}$ inch in four hours.   The work is hardened by plunging it into water while hot.   Small articles are case-hardened by rubbing them when red-hot in powdered ferrocyanide of potassium, re-heating to decompose the powder, and then plunging them in water.

5. **Cast Steel.**—The method of melting blister steel in crucibles and pouring into moulds was introduced by Huntsman in 1740.   Bar iron, carbon, and oxide of manganese or spiegel-eisen are also added to blister steel to produce different qualities.   Cast steel is also made directly in crucibles by melting bar iron with carbon and oxide of manganese, or with spiegel-eisen.   The furnaces are of the usual shape, 3 feet × 18 inches being a common size, and hold two crucibles.   Gas furnaces are also employed, the general arrangement of which is shown in Fig. 76.   The crucibles are made of a mixture

of different clays, burnt clay and coke dust. The bars of blister steel are carefully selected when the best quality is desired, all flushed and aired bars being rejected. If the metal remains too long in the fire it will pour dead, and the fracture will appear scorched. If the metal be too cool, the fracture will be dull in colour and full of pin-holes. Good steel cannot be made from inferior iron, as all elements other than carbon tend to increase the brittleness and the liability of the steel to crack in hardening. Small quantities of other substances are sometimes added when a special property is desired.

Malleable Cast Iron.—Cast-iron articles made of a superior quality of iron, free from sulphur and phosphorus, are embedded in powdered red haematite in an iron box, and heated for a few days at a gradually increasing temperature, and also allowed to cool slowly. The oxide of iron is said to give up oxygen to the carbon of the cast iron, and thus remove it as carbonic oxide. It is more likely that the carbon separates out within the metal. The iron is white to start with, and therefore the carbon is in the combined form; but after annealing, the metal becomes a greyish-white and malleable.

Harveyised Steel Plates.—In this process an armour plate, consisting originally of very mild steel, is cemented in such a manner as to produce a face of very hard steel, the steel becoming gradually less hard from the face to the unaltered soft back. Such a plate of mild steel, containing from 0·10 to 0·35 per cent. of carbon, is placed upon a bed of finely powdered dry clay or sand, deposited upon the bottom of a fire-brick compartment erected within the heating chamber of a suitable furnace. The compartment is then partially filled up with granular carbonaceous material, which having been rammed down upon the plate, is in turn covered with a stratum of sand, and upon this there is laid a covering of heavy firebricks. The furnace is raised to an intense heat, which is kept up for such a period of time as may be required for the absorption by the metal adjoining the upper surface of the plate of an additional 1 per cent. of carbon. The temperature of the heating chamber outside the treating compartment is raised to about that required to melt cast iron, and is kept up for a greater or less length of time, according to the depth of the stratum of steel which it is intended to charge with an excess of carbon.

The following is an example of this process: A plate 10½ inches in thickness, composed of a steel containing 0·35

per cent. of carbon, may be charged with additional quanti-
ties of carbon, gradually varying in amount from about 0·10
per cent. at a depth of 3 inches beneath the surface of the
exposed sides of the plate, to 1 per cent. at the surface, by a
continuance of the treatment for a period of 120 hours after
the furnace has been raised to the required temperature.
The depth to which this increased degree of carburisation
can be allowed to penetrate increases with the thickness of
the plate.   This penetration is dependent not only on the
temperature of the furnace and on the length of time the
plate is exposed to the cementation process, but it is also
greatly facilitated by the continuous firm compression of the
carbonaceous matter against the plate.   The plate, when
sufficiently carburised, is freed from its carbonaceous cover-
ing, allowed to cool to a dull cherry-red heat, and then
hardened.   In this connection it is interesting to note that
such plates hardened by a spray jet gave unequal results on
trial, the upper corners showing resistance to penetration by
shot, while the bottom of the plate was penetrated.   This was
due to the heated water from the cooling of the upper portion
of the plate acting as a protective coating to the lower portion
during the cooling, thus preventing rapid cooling.*

Iron Age, vol. xlviii., p. 736.

CHAPTER XII.

THE BESSEMER PROCESS.

THIS process consists of blowing air through molten pig iron in a vessel termed a converter, whereby the carbon, silicon, and some iron are oxidised. This oxidation produces a high temperature, keeping the mass in a liquid state, and purifies the iron without the aid of ordinary fuel. Two distinct modes of working, employing totally different classes of pig iron, are now adopted. In one the converter is lined with acid material, termed ganister, and in the other a basic lining of calcined dolomite is used—this is termed the basic Bessemer process, while the former is distinguished as the acid process.

Acid Process.—The iron employed must be pure, so far as phosphorus and sulphur are concerned. Molten pig iron from a cupola is run into the vessel while it is in the horizontal position, the amount varying from 3 to 10 tons or upwards. It is then rotated into the vertical position, the blast having been first turned on to prevent the metal running through the twyer holes. During the first five minutes the carbon passes from the graphitic to the combined form, the silicon and manganese, with some iron, become oxidised, and then unite to form a silicate of iron and manganese. Then the carbon begins to burn, the action becomes very violent, the flame is brilliant, and showers of sparks, consisting of carbon, iron, and slag, are ejected by the evolution of carbonic oxide. This lasts for seven or eight minutes. When the last trace of carbon is removed the flame drops, and the iron begins to burn if the blow is continued. The converter is now brought to the horizontal position, and about 10 per cent. of spiegel-eisen, or its equivalent of ferro-manganese is run in, or dropped in in the solid state. The metal is then tipped into the ladle, and run from thence into the moulds.

The duration of the blow will depend on the variety of
pig iron, its quantity, and the pressure of the blast employed.
A feebly siliceous iron will be refined in fifteen minutes, but a
very siliceous one may require thirty minutes. As iron after
decarburisation always contains oxygen, the object of adding
the manganese alloy is to give sufficient manganese to com-
bine with that oxygen, and also with it enough carbon to
convert the iron into steel, if steel is aimed at. The oxide of
manganese combines with some of the silica, and renders the
slag more fusible. The following is an analysis of a sample
of Bessemer slag :

Silica, SiO_2, ...	73·15
Alumina, Al_2O_3, ...	2·54
Ferrous oxide, FeO, ...	20·02
Manganese oxide, MnO, ...	2·65
Lime, CaO, ...	·95
Sulphur, S, ...	·68
	99·99

The following analyses by Snelus give the composition of
the gases given off during the blow :

Name.	Formula.	After 2 min.	After 4 min.	After 6 min.	After 10 min.	After 14 min.
Carbonic acid, .	CO_2	9·96	8·57	8·05	3·58	1·34
Carbon dioxide,	CO	·03	3·95	4·58	19·59	31·11
Oxygen, . .	O	·76	—	—	—	—
Hydrogen, .	H	—	·90	2·00 }	76·83	67·55
Nitrogen, . .	N	89·25	86·58	85·37 }		
		100	100	100	100	100

The iron employed in the acid process must be practically
free from phosphorus and sulphur, as these bodies are
scarcely affected by the blow ; but silicon to the extent of 2
to 3 per cent. is advisable, as it helps to furnish the requisite
heat by its union with the oxygen of the air. When silicon
is deficient the blow is said to be too cold, but this may
be remedied by adding some silicon-iron and increasing the
pressure of the blast. White iron, containing its carbon in
the combined form, yields it up to oxygen, producing car-
bonic oxide at the early stages of the blow, also making
the blow too cold. Bessemer converters are generally so
arranged as to be movable through an angle of 180°, thus

enabling the metal and slag to be poured from the mouth. Figs. 77, 78 represent the usual form of vessel. It consists of a shell of wrought-iron plates riveted together, the neck being included at an angle of about 30° to the axis of the body. The centre of the body is enclosed with a stout iron band, to which is fixed two arms, termed trunnions, by which the vessel is suspended on iron standards. One of these trunnions is hollow to allow for the passage of the blast into the pipe which leads to the twyer box, which is attached to the mov-

Fig. 77.

Blast
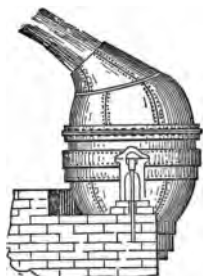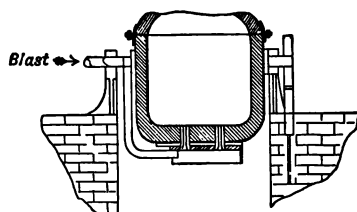
Fig. 78.
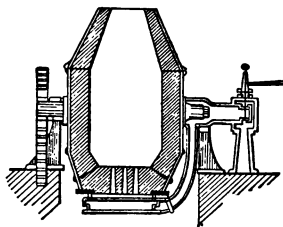
Fig. 79.

able bottom of the converter. The bottom is perforated by ten to fifteen circular holes, in each of which is placed a conical fireclay twyer about 20 inches long, and perforated with ten to twelve holes, each three-eighths of an inch in diameter. The interior lining is of ganister 9 to 12 inches thick. The converter is rotated by means of a rack, carried by the piston rod of a direct-acting vertical engine, or a ram actuated by hydraulic power and gearing, with a pinion attached to the solid trunnion. A newer form of converter, which has been largely used for big sizes, is concentric, as shown in Fig. 79,

so that it may be charged and discharged from either side, and the wear of the lining more equalised. In this figure the tipping gear often consists of a worm wheel 8 feet in
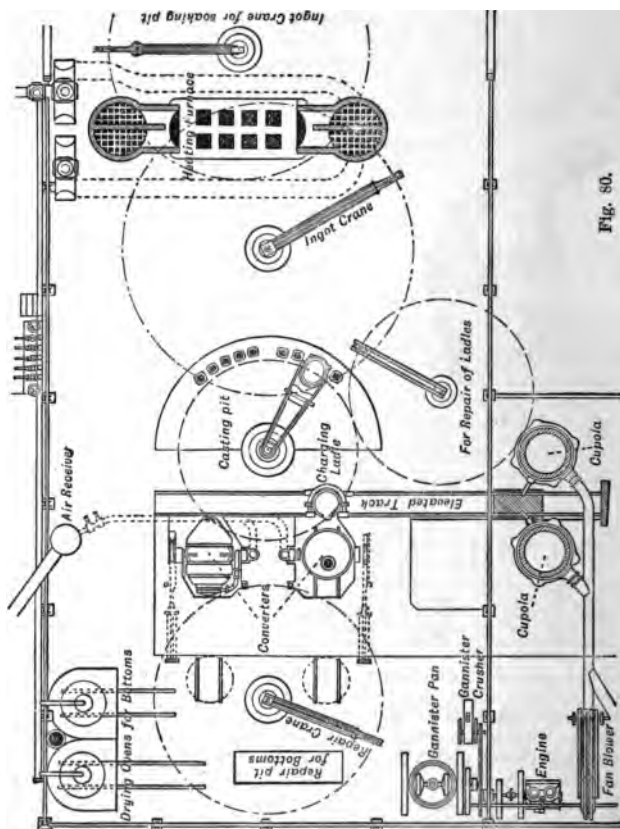
diameter, attached to the belt of the converter and gearing with a screw, which receives its motion from the cranks of a pair of hydraulic engines mounted on one of the standards.

Fig. 80* shows the plan of a good arrangement for a small Bessemer plant. Two cupolas deliver the molten cast iron to a ladle, which runs on an elevated track, and which in turn delivers it to the vessels. An ordinary casting ladle receives the steel, and from it the metal is run into moulds standing along the rim of a semicircular casting pit. From this pit the ingots are drawn by a crane, which deposits them on end in a heating furnace or soaking pit, from whence they are conveyed to the rolling mill. The refractory materials are prepared in a space behind the vessels, and near to this is a small engine which drives the blowers for the cupolas, and actuates the crushing and pulverising machinery for the refractory materials.

Basic Process.—This is used for iron containing phosphorus. In 1835 Berthier showed that in the puddling process phosphorus was removed by the aid of basic slag, and early attempts were made to substitute a basic for an acid lining in the Bessemer converter, but these trials were unsuccessful until Thomas & Gilchrist in 1878 demonstrated its feasibility. Their chief difficulties at first were to get a sufficiently durable lining, but with the aid of Messrs. Snelus, Richards, and others, this difficulty was overcome by adopting one of calcined dolomite mixed with tar, and moulding this into bricks at a pressure of 200 atmospheres. The bottom of the converter is rammed in with the same material, and made nearly red-hot. When a charge is being worked, lime is thrown in and a basic slag is formed, which absorbs any phosphoric acid. White iron rich in phosphorus (1 to 3 per cent.) is preferred, although grey iron may be employed, and, if deficient in phosphorus, a little ferro-phosphorus may be added. In fact, to a great extent, phosphorus in the basic process takes the place of silicon in the acid process.

The mode of working is somewhat similar to that of the ordinary method, but the blow is longer, and after the carbon has burnt off the blow is continued for about two minutes, termed the after-blow, during which the phosphoric acid passes into the slag. Then the vessel is turned into the horizontal position, and a sample of the metal removed and tested by a hammer, and if not malleable the vessel is turned up, and the blow continued for another half a minute, when a further test is made. When the metal is malleable, the ferro-manganese is added. After the addition of the manganese alloy, a little of the phosphoric acid in the slag is decomposed by the carbonic oxide produced, and the phosphorus passes

* Howe, *Metall. of Steel,* p. 327.

into the metal.   The order of combustion and removal of
certain metalloids during the basic Bessemer blow is shown
by Fig. 80A.   It shows that so long as silicon is being
oxidised the phosphorus is not attacked.   The silicon is
removed in about two minutes.   A portion of the carbon is
burnt off at the same time, but very little carbon is oxidised
before the whole of the silicon is removed.   The sulphur
slightly increases till the commencement of the after-blow.
After the carbon has been reduced to a very small amount,
the phosphorus rapidly burns, and is the cause of the high
temperature at the end of the process.   It will be observed
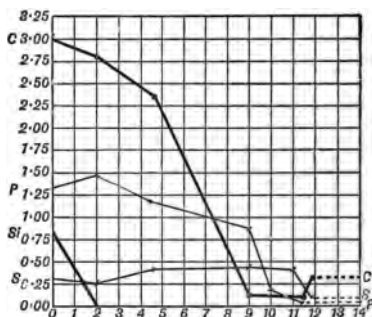
Fig. 80A.

that during the combustion of the silicon the proportion
of phosphorus actually increases.   The composition of the
slag is represented below :

Silica (SiO₂),	.	.	.	.	.	.	.	8·02
Phosphoric acid (P₂O₅),	.	.	.	.	.	.	17·15
Ferrous oxide (FeO),	.	.	.	.	.	.	9·04
Manganese oxide (MnO),	.	.	.	.	.	6·27
Lime (CaO),	.	.	.	.	.	.	56·03
Magnesia (MgO),	.	.	.	.	.	.	3·20
Sulphur (S),	.	.	.	.	.	.	·29

$$100·00$$

It is stated that the phosphorus exists in the slag as a tetra-
basic phosphate of lime (4CaO.P₂O₅).   This slag is used as a
manure, and in admixture with tar as a lining material for
re-heating and open-hearth furnaces.

The ladle (Fig. 81) used in steel works is made of wrought iron or steel, and lined with a similar substance to that of the furnace. The tap hole is at the bottom, and is closed or opened by the stopper (*a*), the opposite end of which passes through a slide bar (*b*) on the outside, which is worked by a hand lever. This ladle is generally suspended on a movable platform, and is provided with gearing for tipping out the slag.

The moulds are made of cast iron, open at both ends, tapering towards the top to facilitate the removal of the ingots. The moulds are generally filled from the top, then sand is thrown on the surface of the metal, and the lid tightly secured, so as to ensure sound ingots. Sometimes a group of moulds is filled from the bottom, being arranged round a large one in the centre, into which the metal is tapped. From the bottom of this run feeding tubes of fire-clay, opening upwards into each member of the group.
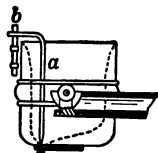
Fig. 81.

Fixed Converters.—These are generally of small dimensions, and the blast is introduced at the side instead of at the bottom. Howe summarises the defects of fixed converters thus: (1) They do not readily permit of bottom blowing, hence greater loss of iron during conversion, and a faulty twyer would be liable to spoil the whole charge, while in a movable vessel the metal could be easily tilted away by its rotation. (2) In side blowing the charge must all be tapped if a twyer becomes faulty, and the metal is then simply scrap. (3) The metal has to be tapped instead of poured, and the proportion of carbon is less under control because the time of tapping is longer than that of pouring. (4) Only mild steel or ingot iron can be made, because the recarburisation cannot be done in the vessel, and the manganese alloy is therefore added to the ladle. The following is a type of this class of converter:

Clapp & Griffiths' vessel.—The ordinary converter is about 5½ feet internal diameter and 10 feet high, lined with silica bricks, and provided with from four to six horizontal twyers, fitted with valves for regulating the blast. The twyers are arranged about 9 inches above the floor of the converter, and about 5 inches below the surface of the metal when charged, which enable a soft blast of 5 or 6 lbs. per square inch to be used. As the slag rises, it is run off through a slag-hole during the intermediate stages of the blow. At the con-

clusion the metal is tapped as from a cupola. Ferro-manganese is then added to the metal in the ladle to form mild steel or ingot iron.

The Robert Converter (Fig. 82), although a movable one, is only adapted for small charges, varying from 1 to 3 tons. The blast is introduced near the upper surface of the
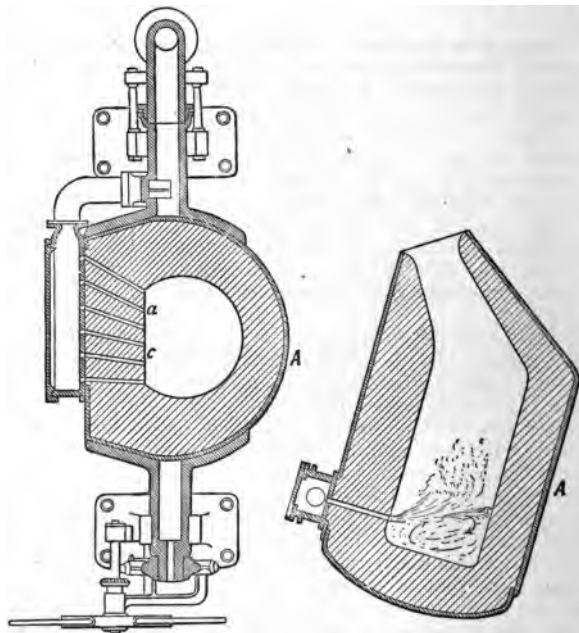
Fig. 82.

metal, and the twyers inclined at different angles, so as to give the metal a rotatory motion. The vessel itself is tilted during the first half of the blow, and turned more vertically as the operation proceeds, in order that the blast may be less strongly localized. This converter is mounted on trunnions and revolved in usual way, but by means of hand gearing. The chief advantage of small converters is that they enable small users to manufacture their own steel.

OPEN-HEARTH PROCESS.

This process is conducted in a Siemens regenerative furnace, and comprises three modifications: (1) pig and scrap process; (2) pig and ore process; (3) a combination of the two former, which is now generally adopted, and termed the Siemens-Martin process.

The first or Martin process consists of melting malleable iron with pig iron, preferably one low in silicon and containing manganese. When the charge is melted it may be kept in fusion, because the intensity of the oxidising action may be easily maintained. In order to hasten the operation, the pig iron is charged into the furnace in the liquid state and speedily raised to a white heat; the malleable iron, previously made red-hot, is then added in lumps. With a neutral flame, No. 1 grey pig will dissolve 9 times its weight of Bessemer scrap, while No. 3 pig will not dissolve more than 4 times its weight, and, when the flame is oxidising, considerably less. The oxide of iron Fe_3O_4, formed by oxidation, reacts on the carbon of the pig iron, producing carbonic oxide, which, on escaping, agitates the bath of metal, and thus tends to make it uniform in composition. When the whole is melted a test is taken, and when the metal shows the proper fracture and toughness as well as the right degree of decarburisation by Eggertz' test, it is run into a ladle and cast into ingot moulds, as in the Bessemer process. This method of working is only possible with the best pig iron, so that the usual plan is to completely decarburise and then add spiegel-eisen or ferro-manganese. The latter containing more manganese, a less quantity is required for deoxidation, and as therefore less carbon is added a milder steel is produced than when the former is employed.

The second or Siemens process is worked with pig iron and pure rich oxides, the latter replacing the scrap iron of the Martin process. In the latter the iron takes up carbon from the pig iron, but in the Siemens method the oxide of iron assists the atmosphere in its oxidising action. It partly removes the silicon, manganese, and carbon, so that the process is hastened and the material used is less costly. The difficulty has been to make the light ore thoroughly penetrate the denser metal. This difficulty has been partly avoided by adding the ore in small portions at intervals. The weak point of this method is the corrosive action of the basic oxide on the lining of the furnace, forming an acid silicate of

iron, which increases the amount of ore used, especially when a large portion is added at one charge.   At Landore the charge of ore and pig was added cold, and 8 to 12 per cent. of ferro-manganese or spiegel was added at the conclusion as usual.

The third modification, or Siemens-Martin process, is similar to the Siemens method in the mode of working.   Pig iron is
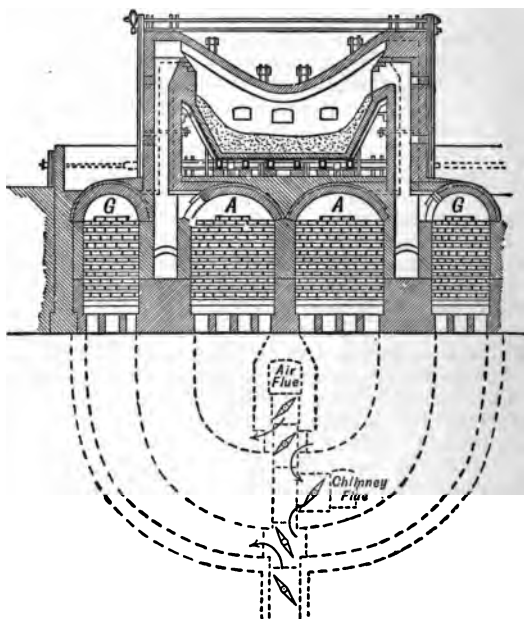
Fig. 82A.

first charged into the hot furnace, and then iron and steel scrap is added in small quantities at a time, and a certain quantity of rich oxide of iron.   Spiegel or ferro-manganese is added at the conclusion.

In the three modifications as above described, it has been assumed that the pig iron contains but little phosphorus and sulphur.   These elements are only to a small extent removed

by the process, in consequence of the siliceous nature of the slag, which is but feebly oxidising, so that phosphate of iron could have but a temporary existence.

The Siemens open-hearth furnace is of the reverberatory type, having a slightly concave bed lined with sand, which has been well rammed in and strongly heated. The bed also slightly inclines towards the tap hole, which is situated beneath the middle working door on the front side of the furnace. The roof is lined with Dinas brick. In the later forms of this furnace (Figs. 82A, 82B) the roof has a strong slope from each side to the centre, giving a very plunging flame ; the air space beneath the bed is enlarged, the gas ports are longer and narrower, and the regenerators are
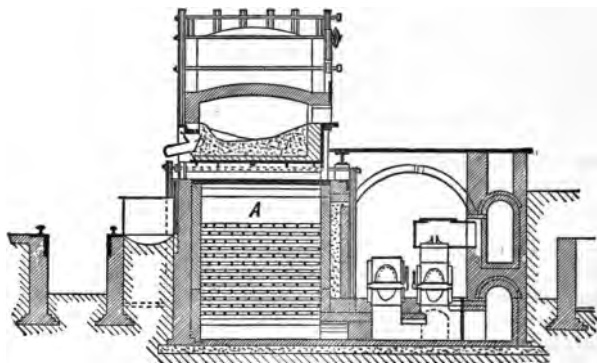
Fig. 82B.

larger and roofed with semi-circular arches, so as to give a larger exhaust flue for the flame, and thus modify its temperature before it reaches the regenerators. The furnace has three doors, the outer ones being used for charging and the middle one for working. The dotted lines below the furnace indicate the valve arrangement and the flues, through which the gas and air pass through the pairs of regenerators alternately. It will be noted that the air regenerators are larger than those used for the gas. The reversing valves are simple flaps acting like a four-way cock, and actuated by means of levers. The modern furnace is of much greater capacity than the early one, 10 to 15 tons being now often treated in one charge.

The charge consists of good hematite pig iron of the grey variety, and various kinds of scrap iron and steel, which must be nearly free from phosphorus. To this is added about 2 tons of hematite in a 10-ton charge. This causes a vigorous boiling ; and as the oxide of iron is partly reduced in the furnace, the yield of steel is in excess of the pig and scrap added. In addition to the introduction of ferro-manganese or spiegel-eisen at the finish, mentioned above as necessary for the removal of oxygen and to impart the required amount of carbon, it is customary to add a little aluminium to the metal in the ladle, so as to keep it more fluid during the time of teeming into the moulds. The consumption of fuel is about 15 cwts. per ton of steel produced.

Pernot's Furnace, with movable bed, already described as used in puddling iron, is also used for making steel (see Fig. 63, p. 158). The inclination of the bed and the rotation of the furnace cause a more energetic oxidising action than occurs in the Siemens furnace, so that less scrap and ore are necessary for the charge. At St. Chammond the pig iron is charged after being heated to redness, and the steel or iron scrap is added cold at the same time. The bed is made to rotate three or four times per minute during charging and working. The pig iron melts first and forms a liquid bath, and the scrap is alternately exposed to the action of the air and molten metal by the motion of the bed. The pig iron is thus uniformly oxidised by the oxide of iron Fe_3O_4 formed at each revolution, when the unmelted iron is exposed to the air : the iron thus acts as a vehicle for oxygen.

It is claimed for this method that with a 5-ton charge, five operations may be completed in twenty-four hours, each charge only requiring 7 cwts. of coal, and $1\frac{1}{4}$ cwts. for the preliminary heating of the pig iron. The charge consists of one-fifth pig iron and four-fifths crop ends of rails, etc. At the conclusion of the refining, spiegel-eisen or ferro-manganese is added as in the Siemens process.

Ponsard has modified the Pernot furnace by the addition of two twyers inserted in the side lining. These twyers work alternately, with the object of hastening the first part of the process. The bed only moves half a revolution, since in a complete revolution the twyers would be alternately in and out of the metal. The central spindle upon which the hearth rotates is made hollow, and through this passage the blast passes to the twyers. This method then is a combination of the Bessemer and Siemens systems of making steel.

In Sweden, where wood fuel is largely used, a special type of gas producer is necessary in connection with the open-hearth furnace, and the latter of late years has been built with a high roof, domed arch, and with alternating or " gallery " ports for gas and air.   By this means the pig iron is partly melted in the hot-air currents, coming from the ports, and the silicon and carbon are partly oxidised during the fusion.   Fig. 83 shows a 10-ton furnace.   It has been found when sulphurous fuels have been used that the metal is less liable to take up sulphur during the melting when gallery ports are used, instead of having gas ports below and air ports above.   The ports incline downwards to the hearth. 88 cubic feet of regenerator space per ton of steel is allowed. The valves are American lift-and-drop dish valves, which rest against water-cooled seats.   The air regenerators are the same size as the gas regenerators, as gas from wood and peat is colder than gas produced from coal.

Three kinds of steel are made : (1) Mild steel containing ·15 per cent. carbon ; (2) tool steel with upwards of ·40 per cent. carbon ; (3) steel castings.   For No. 1 variety, pig iron practically free from sulphur is used, and the scrap iron is selected so as to be free from rust, as rust may contain sulphur.   The pig and scrap are charged at the same time, and when melted the requisite ore is added.   The main object is to obtain soft metal as free as possible from sulphur and oxygen, so that little ferro-manganese is required to be added.   For telegraph wire no manganese should be in the steel.   Wood fuel is an advantage where the sulphur is required to be very minute.   If the charge becomes too cool during the working, the metal will be red-short.   ·25 per cent. of manganese is said to decrease the toughness more than ·04 per cent. of phosphorus, which is the highest amount admissible in first-class steel.   If the charge gets too hot silicon will pass into the steel.

In the manufacture of tool steel in the acid-lined furnace, phosphorus must be practically absent, and fuel as free as possible from that element is therefore used as well as good quality pig-iron and scrap.   The process is so conducted that a good steady heat is maintained, so as to get metal nearly free from gases during tapping, and hence ingots free from blow-holes without too much tendency to " pipe."   The great danger in making hard steel is in getting it too hot, which produces surface blow-holes.

In making steel castings it is essential that the moulds should be made of proper material.   A mixture of red sand-

Fig. 88.

stone and best quartz is used, ground to the requisite degree
of fineness. A special preparation for facing the moulds
consists of the German *kieselguhr* mixed with glue. In order
to save the expense of keeping so high a temperature during
the melt, a minute quantity of aluminium is added before
tapping. Aluminium cannot be used in steel where the
highest quality is desired, as it causes crystallisation ; but
this is to some extent destroyed by annealing. Aluminium,
even in small quantity, diminishes the toughness of best
steel.*

Open-hearth Basic Process.—The object of a basic
lining, as in the Bessemer converter, is to enable common pig
iron, containing phosphorus and sulphur, to be used. The
fixed lining of calcined dolomite and tar, and the addition of
lime to the charge causes a highly basic slag to be formed,
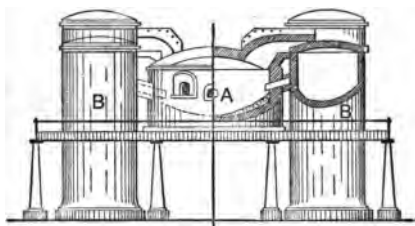
Fig. 84.

which takes up a portion of the phosphorus and sulphur as
well as the silicon. In the basic Bessemer process the phos-
phorus largely passes into the slag during the "after-blow,"
when the carbon is reduced to a minimum, so that this after-
blow, with the consequent loss of iron, seems essential. In the
Siemens furnace this refining influence is absent, and Gruner
states that, unless a similar contrivance be adopted, such as
Ponsard's, it is doubtful whether mild steel, free from
phosphorus, can be produced from common phosphoric
pig iron.

Dick's Open-hearth Furnace.—This furnace, Fig. 84,
is the same in principle as the ordinary Siemens furnace, but
differs in the nature of the lining and in the construction
and arrangement of the various parts. The furnace or

* Erik Gison, Amer. Inst. Mining Engineers, 1894.

melting chamber (A) consists of a circular or oval body with an iron or steel casing. It is placed on a platform supported by girders, and left entirely clear underneath, so that the bottom is kept cool and the lining better preserved. The four regenerators (BB) form four circular towers, and instead of being situated below the bed of the furnace, are placed in pairs at opposite sides of the furnace. Each regenerator forms a separate structure, which is out of harm's way in case of the metal breaking out, and as it has only its own weight to carry it cannot get out of shape. It is very desirable to regulate the relative amounts of the heated gases passing through the regenerators, in order to control the
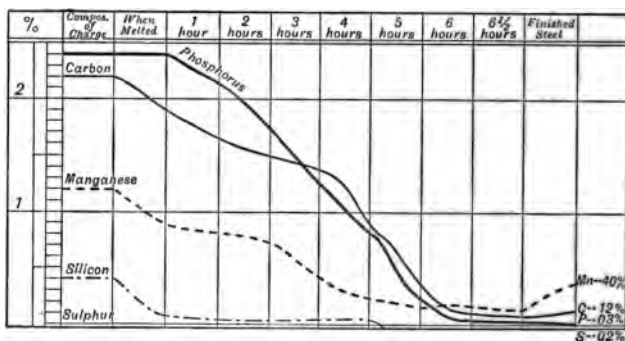
Fig. 85.

relative amounts of heat stored up in these chambers. The tendency is for the gas chamber to receive the largest share of the waste heat, whereas the air chamber should be the more highly heated of the two. This is effected by the adoption of a new kind of disc-valve.

This class of furnace is worked with a basic lining for the bed and a lining of silica bricks for the roof, which is suspended from girders so as not to rest on the sides of the hearth, a space of about a quarter of an inch being left between the basic and the acid linings. An opening at the side of the furnace allows the inflow of heated gas; and directly over this is an opening in the roof for admission of the hot air.

Mr. Darby of Brymbo* uses a 20-ton basic open-hearth furnace, and the charge consists of 80 per cent. pig and 20 per cent. scrap steel or wrought iron, with the addition of limestone to form a basic slag. Any kind of iron may also be used in the steel furnaces, provided the silicon is low, and the phosphorus is immaterial since it is taken up by the lime.

The diagram, Fig. 85, shows the order in which the various impurities are eliminated in the basic open hearth.

Steel Casting.—The operation of pouring molten steel requires great care so as to get compact and weldable ingots. The higher the temperature of the liquid metal the more gas it absorbs, and as the temperature falls the absorbed gases are liberated ; if, however, the steel be poured at too high a temperature some of these gases will remain after the surface has solidified, and produce a honeycomb structure ; the cavities are termed "blow-holes."

"Glazed" iron (which is iron containing silicon) and a triple compound of iron, manganese, and silicon, termed "silicon-ferro-manganese," are now largely used for adding to molten steel to produce sound ingots. With regard to this subject, Mr Pourcel says : "On analysing a sample free from blow-holes, silicon is always found ; whilst a honey-combed sample contains interposed slag, but no free silicon."

Silicon is more oxidisable than carbon, so that solid silica SiO_2 may be formed instead of gaseous carbonic oxide CO. Moreover, silica forms with oxide of iron and oxide of manganese a fluid slag which largely liquates out when the steel solidifies. This is especially important in basic steel where the ordinary slag is less fusible, since it is the slag between the molecules which makes the steel red-short. The two reducing bodies, manganese and silicon, act simultaneously in reducing the oxide of iron formed while the liquid metal is exposed to the air.

Müller considers that silicon acts by increasing the solvent action of steel, which then retains the gases in solution instead of being liberated. He also suggests that the beneficial effect of adding spiegel-eisen is partly due to the evolution of carbonic oxide which ensues, sweeping out some hydrogen at the same time, thus reducing the liability to blow-holes. The different opinions as to the cause of blow-holes may be summarised as follows : 1. By gases in solution. 2. By gases formed by the action of the air on the metal

* *Journal Iron and Steel Inst.*, No. 1, 1889.

during pouring. 3. By air and gases carried into the metal mechanically when the metal is being run into the moulds, the viscous mass preventing them from escaping.*

In large complicated castings due allowance must be made for contraction, for steel contracts twice as much as cast iron, therefore large castings are often made in two or more pieces to avoid internal strains. In consequence of the contraction, steel castings have often been destroyed when left in the moulds to cool. They should be removed as soon as possible and placed in the annealing furnace while hot, since the re-heating of cold castings is injurious, especially in large work. Tempering in oil is occasionally resorted to, which raises the tensile strength and increases the elongation, but diminishes the ductility.

Various devices have been introduced for consolidating steel ingots and diminishing the injurious effects of blow-holes. Mushet cast a head of metal on the ingot by means of a clay tube. Whitworth & Co. submit the metal while fused to great pressure by means of• a powerful hydraulic press. The mould is lined with refractory material and con-structed so as to allow of the free escape of gases during the compression. Mr. Jones of Pittsburg admits high pressure steam at the top of the ingot. A steam drum is fixed to the ingot crane having a number of cocks and india-rubber con-necting pipes corresponding to those of the moulds. When the moulds are filled, caps are fastened on and steam admitted for five minutes at a pressure of 80 to 150 lbs., mild steel requiring the higher pressure. The steam cools and her-metically seals the tops of the ingots, and also consolidates the steel, probably by ejecting the enclosed gases. Krupp of Essen uses liquid carbonic acid instead of steam. Very strong iron bottles containing the liquid under great pressure are connected with the feeding hole, and when the cock is opened the expansion of the acid, in changing from the liquid to the gaseous state, exerts a pressure of 52 atmospheres. By heating the bottle to 200° C. previous to opening the cock the pressure is increased to 800 atmospheres.†

Treatment of Steel Ingots.—Steel is not piled like iron for re-heating, but cast into an ingot of the proper size for the production of the required bar, plate, rail, etc. The hot ingots are usually conveyed from the moulds to a re-heating furnace (see Figs. 70-72), and were formerly extended by the steam hammer before rolling, but this is considered objectionable, and they are now passed directly through the

* See *Steel*, by Howe, § 210, p. 134.   † *Ibid.*, § 229, p. 155.

"cogging" or roughing rolls, then re-heated and rolled in the finishing rolls to the required section. For rails, the blooms after "cogging" are finished right off without re-heating, being rolled in long lengths and then cut into rails of the required length by circular saws. This reduces the amount of waste from the crop ends, as a fewer number of rough ends require to be cut off, than when the rails are made in short lengths.

CHAPTER XIII.

SILVER.

DR. PERCY in his work on Silver, expresses his opinion that the Metallurgy of Silver is the most extensive, the most varied, and the most complicated of all the branches of Metallurgy. The metal has been known and used from remote antiquity, its pure white colour and brilliant lustre, together with its great malleability and ductility, have caused it to be prized as one of the most valuable of metals. The principal silver producing countries are the United States, Mexico, Chili, Peru, and Canada. It is also largely produced in certain parts of Europe.

The properties which make silver so valuable are its pure white colour, for when an ingot is broken the fractured surface rivals snow in whiteness; but when it is precipitated from its solutions it is very often of a grey colour, due to the fine state of division of its particles. It is a soft metal, being but a little harder than gold. It is sonorous when struck. It is extremely malleable and ductile, and is only exceeded by gold in this respect; it may be hammered into leaves $\frac{1}{10000}$ of an inch in thickness, and Percy says a single grain may be drawn into a wire 400 feet long. Its tenacity is 7·1 tons per square inch, it elongates 33 per cent. before rupture, and may be considerably increased by mechanical treatment, such as drawing it into wire, etc. Aitken gives the tenacity of a wire $\frac{1}{10}$ inch in diameter as 13·64 tons per square inch. Its specific gravity is 10·53 in the solid and 9·46 in the liquid state, and its specific heat, ·056. Its co-efficient of linear expansion is ·0000192. It is the best conductor of heat and electricity known, but this property is greatly interfered with by the presence of impurities. Its melting point is 945° C. and at the temperature of the electric arc it may be readily volatilised from one lime crucible to another.

At 1330° C. it volatilises in a current of hydrogen, and at still lower temperatures it is partly volatilised if easily volatile substances, such as zinc and arsenic, are present. It is without taste or odour.

Silver assumes certain allotropic forms, as shown by Carey Lea, when reduced from its solutions by certain organic salts, such as a mixture of ferrous sulphate and sodium citrate. It may be ruby red, blue-green, reddish brown, or copper coloured. All these forms are brittle and readily changed by acids, and in some cases by friction, to normal silver.

Chemical Properties of Silver.—The metal does not oxidise in air under ordinary conditions, even when heated, but when it is melted on charcoal under a jet of oxygen it burns with a blue flame, and according to Vauquelin, vapours of oxide are produced. It may also be oxidised by ozone. Certain oxides, such as those of copper, lead, antimony, and arsenic, when ignited with silver produce some silver oxide, and probably a little silver is oxidised in the process of cupellation. Silver undergoes no change when heated with alkaline nitrates and similar oxidising bodies, or with caustic alkalies. When silver is kept melted for some time in presence of air it absorbs oxygen and keeps it in solution until on the point of solidifying, when the gas is suddenly liberated if the metal is cooled quickly, producing an excrescence on the surface and violently projecting small particles into the air. This is termed " spitting." In this way silver may absorb 22 times its volume of oxygen. and may retain half its volume in the occluded state. Silver may be oxidised by copper sulphate, lead sulphate, and copper nitrate. On the other hand silver oxide precipitates many metals, from their solutions as oxides, such as those of manganese, nickel, lead, etc. Silver oxide has the formula Ag_2O.

Silver and sulphur combine by direct union when melted together, forming silver sulphide Ag_2S, which is a dark-grey crystalline body, somewhat soft and malleable. It is unchanged by the atmosphere at ordinary temperatures, but at a red heat it is decomposed into metallic silver and sulphur, which latter unites with oxygen, forming sulphur dioxide SO_2. Most other sulphides, when heated in air, form either sulphate or oxide, but this is not the case with silver sulphide, unless other sulphides, such as those of copper and iron, are also present. It is decomposed when fused in the presence of iron, lead, and copper, and is also largely decomposed by steam and by hydrogen. Silver

sulphide is one of the most important silver compounds, and plays a very prominent part in the metallurgy of silver, forming one of its chief ores. Silver sulphide is decomposed by chlorine, silver chloride being formed.

Silver Chloride AgCl is formed by the action of chlorine gas or chlorine water on silver. It is also produced by precipitation from silver solutions with a soluble chloride or with hydrochloric acid. The precipitate is soluble in a saturated solution of common salt, or in a solution of potassium cyanide, or in that of sodium thiosulphate, or in ammonia. It is reduced by hydrogen, by metals, such as zinc, and by alkaline carbonates. Various wet methods for the extraction of silver from its sulphide and other ores depend on the formation and reduction of silver chloride, and the metal is often converted into this form before reduction by the amalgamation process. The bromide and iodide of silver are formed by direct union of the elements or by precipitation from silver solutions by means of potassium bromide or iodide.

Silver and Cyanogen. Silver cyanide is produced when silver is precipitated from its solutions by means of potassium cyanide, but this precipitate is soluble in excess, forming a double cyanide of silver and potassium. This is largely used as a solution for silver plating.

Silver is soluble in nitric or sulphuric acid, and advantage is taken of this in parting silver from gold. If phosphorus is immersed in a solution of silver nitrate the metal is reduced, and by this means it may be deposited on any article covered with a film of phosphorus. This method is used to convert non-conducting bodies into conductors for the purposes of electro deposition.

Silver Ores.—The ores of silver may be divided into two classes, viz. : those in which silver is the chief constituent and those in which silver is present with ores of other metals, which is commonly the case with lead ores, and very frequently with those of copper, zinc, and iron. Of the ores of silver proper the annexed table shows their chemical composition and general properties.[*]

Silver ores occur in lodes traversing gneiss, mica schist, clayslate, etc., and are generally associated with blende, pyrites, spathic iron ore, brown hæmatite, earthy carbonate, heavy spar and quartz. Native silver occurs in laminated or filamentous masses and in grains mixed with other minerals, and sometimes crystallised in cubes, octahedra, etc., and has a silver-white colour. The colour of the other ores enumer-

[*] Thorpe's *Dic. of App. Chem.*; Article, "Silver."   .

Name.	Formula.	Percentage of silver when pure.	Lustre.	Streak.	Specific Gravity.
Native silver, ...	Ag,	—	—	—	10·1 to 11·1
Stephanite, ...	$5Ag_2S$, Sb_2S_3,	68·3	Metallic,	Iron black,	6·3
Stromeyerite, ...	Ag_2S, Cu_2S,	53·1	do.,	do.,	6·3
Pyrargyrite, ...	$3Ag_2S$, Sb_2S_3,	60	Adamantine,	Brown-red,	5·7 to 5·9
Proustite, ...	$3Ag_2S$, As_2S_3,	65·4	do.,	Red,	5·4 to 5·6
Tetrahedrite, or Fahl ore, . . .	—	Up to 30	Metallic,	Grey, black,	4·5 to 5·2
Polybasite, ...	$\{(Ag_2S,CuS)_9 + (Sb_2S_3, As_2S_3\}$,	64·72	do.,	Iron black,	6·1 to 6·3
Horn silver, ...	$AgCl$,	75·25	Resinous,	Light grey,	5·3 to 5·6
Bromargyrite, ...	$AgBr$,	57·44	do.,	Yellow,	5 to 6
Iodargyrite, ...	AgI,	46	do.,	Yellow-green,	6 to 6·5
Amalgam, ...	$Ag_x + Hg_y$,	—	Metallic,	Grey-white,	9·7 to 10·8
Tellurides, ...	Ag_3Te,	—	do.,	Grey, black,	7·5 to 9·4
Argentite, ...	Ag_2S,	87·1	do.,	Dark grey,	7·2 to 7·4

ated in the above table, is generally much the same as that of the streak. The halogen compounds of silver are soft, waxy-looking bodies, easily sectile, readily fusible and easily reduced when heated on charcoal with the aid of a blowpipe. Amalgam is a brittle, silver-white mineral of variable composition ; one has the formula $AgHg$ and another $Ag_{13}Hg$. Tetrahedrite or Fahl ores are names given to complex ores consisting of sulphantimonites and sulphursenites of silver and copper, and containing iron, tin, lead, mercury, etc. The usual amount of silver varies from 2 to 10 per cent. Silver is often found in galena and other ores in sufficient quantity to allow for its profitable extraction, which can be done when the silver does not exceed 4 to 5 ounces to the ton of lead.

<center>METHODS OF EXTRACTION.</center>

The widespread distribution of silver ores and the very varied nature of the minerals in which they occur make it impossible to profitably reduce and separate the metal by any one process, so that the method employed will depend upon the nature of the ore, and to some extent on the locality where it is obtained. In the great majority of cases, enormous masses of material have to be treated to obtain a very small quantity of silver. The various methods may be classified thus .

1. *Amalgamation with Mercury;* in heaps as in Mexico, and in pans, as in the United States and in Europe.
2. *Wet Methods;* as in Europe and America, of which three may be mentioned—Augustin's, Ziervogel's, and Von Patera's.
3. *Lead Methods.* In these the silver is concentrated in a quantity of lead and then cupelled, as in the Liquation process ; or it is smelted with ores of lead, copper and iron pyrites, etc., the product being afterwards cupelled, or subjected to wet processes.

Amalgamation in Heaps.—The treatment of silver-bearing ores with mercury depends on the power of mercury to decompose certain compounds of silver and to dissolve the liberated metal in an excess of itself, forming a solution from which, after the excess of mercury has been filtered off, the silver may be isolated by submitting the amalgam to sufficient heat, in a closed retort or vessel, to expel the mercury, which is condensed in a cool receiver. The Mexican *patio* method is employed for the treatment of sulphur ores containing silver and small quantities of silver chloride, bromide, and

iodide, and certain complex bodies, yielding on an average ·25 per cent. of silver. The ores most suitable are simple or complex sulphides, not containing much galena and blende, not more than 4 per cent. of copper pyrites, and very little of the haloid salts of silver, such as silver chloride.

The ores are hand picked, broken small with rough stamp batteries, and then ground to a fine powder in a circular space, paved with stone, 12 to 15 feet in diameter and 18 inches deep, termed an " arrastra " or " tahona." In the centre of the pit is pivoted a vertical beam supporting four radial arms, to each of which are tied heavy stone blocks; these are made to revolve by means of mules attached to the longer extremities of two of the arms and by the revolution grind the ore with a little water into a fine mud. If free gold and silver, or halogen compounds of silver, are present, mercury is added to dissolve the precious metals.

The ground ore is conveyed in barrels to a circular paved space 40 to 50 feet in diameter termed a " patio." The ore is spread out to a thickness of about 1 foot, and thoroughly mixed with 3 to 5 per cent. of common salt by being continuously trodden by mules driven round the " torta " for an hour. It is then well turned over by workmen and the treading repeated. (Mechanical mixers have been tried but have not come into general use.) The next day " magistral " (roasted copper pyrites) is added ; this is scattered uniformly over the heap and mixed with shovels, and stirred at intervals for several days. Mercury is then added and the mass trodden as before by mules for about two hours. A hot solution of copper sulphate is then added and some copper precipitate, when the mixture is again trodden by mules for a few days. Fresh mercury is then sprinkled on the mass and thoroughly mixed with the charge as before. The whole mixture is transferred to circular stone vats, mixed with more mercury, and water added. The whole is then well agitated by a revolving paddle turned by mules. Water is allowed to run through the vat the whole time. By this means the mercury and amalgam settle to the bottom, and the lighter matters are washed away. The whole of the amalgam is then squeezed in canvas bags, by which means the free mercury is forced through the meshes, leaving a pasty amalgam containing about one-sixth its weight of silver. This is then compressed into cakes which are placed on the shelves of an iron stand, which is covered with an iron bell, suspended by a chain from above. The lower edges are luted down to prevent

escape of mercury. The whole is fixed in a brick chamber in which a charcoal fire is made, and the heat from which volatilises the mercury, leaving a spongy mass of silver. The mercury is condensed in a tank beneath the bell, which is open at the bottom. The reactions are generally explained by assuming that the common salt converts the copper into chlorides, which react on the sulphide of silver, forming silver chloride, and the latter is then decomposed by mercury. The liberated silver then amalgamates with the free mercury. The following equations represent this view of the chemical changes :

$$2NaCl + CuSO_4 = CuCl_2 + Na_2SO_4.$$
$$2CuCl_2 + Hg_2 = Cu_2Cl_2 + Hg_2Cl_2.$$
$$2CuCl_2 + Ag_2S = 2AgCl + Cu_2Cl_2 + S.$$
$$2Cu_2Cl_2 + Ag_2S + 3O = 2AgCl + CuCl_2 + 3CuO + S.$$
$$2AgCl + Hg_2 = Ag_2 + Hg_2Cl_2.$$
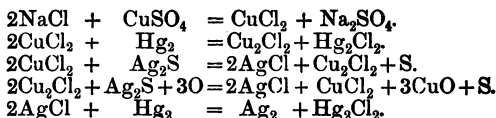
Mr. Bowering denies that silver chloride is formed at all, as he found none in the torta by frequent analyses extending over several months. He is of opinion that silver sulphide and common salt or copper sulphate have no action unless these three compounds are present together. Then the mercury and copper combine with chlorine, forming mercury chloride, cuprous chloride, and sodium sulphate. The chloride of copper has the power of absorbing oxygen, and then decomposing silver sulphide with the formation of metallic silver.

Amalgamation in Barrels.—This method was adopted for the treatment of sulphides, regulus, speise, and black copper containing silver.

The ore is first ground, sifted, and put through a drying furnace, then roasted in a reverberatory furnace with 10 per cent. of common salt. Some of the sulphur and arsenic is expelled and the sulphides oxidised, first to sulphates, then to chlorides. The roasted product is ground to a fine powder, and 10 to 14 cwts. put into an oaken barrel containing scrap iron, and partly filled with warm water. The barrel is then made to revolve, by which means the iron acts more perfectly on the silver and copper chlorides, reducing them to the metallic state. After revolving two hours, 3 to 5 cwts. of mercury and a little copper sulphate are added, and the revolution continued for eighteen to twenty hours. If the ores are very rich, scrap copper is used instead of iron. When the amalgamation is complete the barrel is filled with water and slowly revolved for an hour, and the amalgam

which settles at the bottom, is run off. Fresh mercury is then charged in, and the barrel slowly rotated in order to collect any amalgam that may have been retained in the pulp. This is then run off, and the contents of the barrel discharged. The amalgam is washed, strained, and the mercury volatilised from the amalgam in an iron retort. Each barrel is about $4\frac{1}{2}$ feet long, $4\frac{1}{2}$ feet wide. The charge is 2000 lbs. of ore, and 100 lbs. of scrap iron. This system, known as the European method, is but little used at the present time.

Amalgamation in Pans.—The old "cazo" or caldron process for amalgamating silver was introduced by Barba into South America, in what is now Bolivia, in 1609. It may be considered as a connecting link between the patio and the modern pan processes. The ores most suitable for the cazo method are the haloid salts of silver, such as the chloride, but sulphides are unsuitable. These haloid compounds are decomposed mainly by copper, and assisted by the solvent action of common salt. Cupric chloride $CuCl_2$ is first formed and afterwards converted into cuprous chloride Cu_2Cl_2 by contact with mercury and metallic copper. The caldron employed is a copper vessel, or wooden vessel with a thick copper bottom. Within this vessel is placed a stirrer which is rotated by means of a mule.

The ores are first crushed and ground to a fine powder, and introduced into the caldron with a sufficient quantity of water to form a fine mud. The contents are then heated to boiling by means of a fire underneath the copper bottom, and 10 per cent. of common salt and some mercury added. The stirring is now commenced by setting the mule in motion, and continued for about an hour, when an assay is made, and if the amalgam is crystalline and of a grey colour, fresh mercury is added, and so on at intervals for about six hours. When the amalgamation is completed, the muddy liquor is drawn off and the heavy deposit on the bottom ladled out. It consists of oxidised compounds of lead, iron, etc., and a powdery silver amalgam. The latter is washed, with the addition of fresh mercury, and the resulting amalgam treated as described in the previous processes, by pressing and retort-ing. The resulting silver generally contains some copper, which is separated by cupellation. The consumption of mercury is less than in the Mexican method. If sulphides are present with the chlorides, then the residues after amal-gamation are treated by the patio process. This method is still employed at the large Huanchaca mine in a modified form.
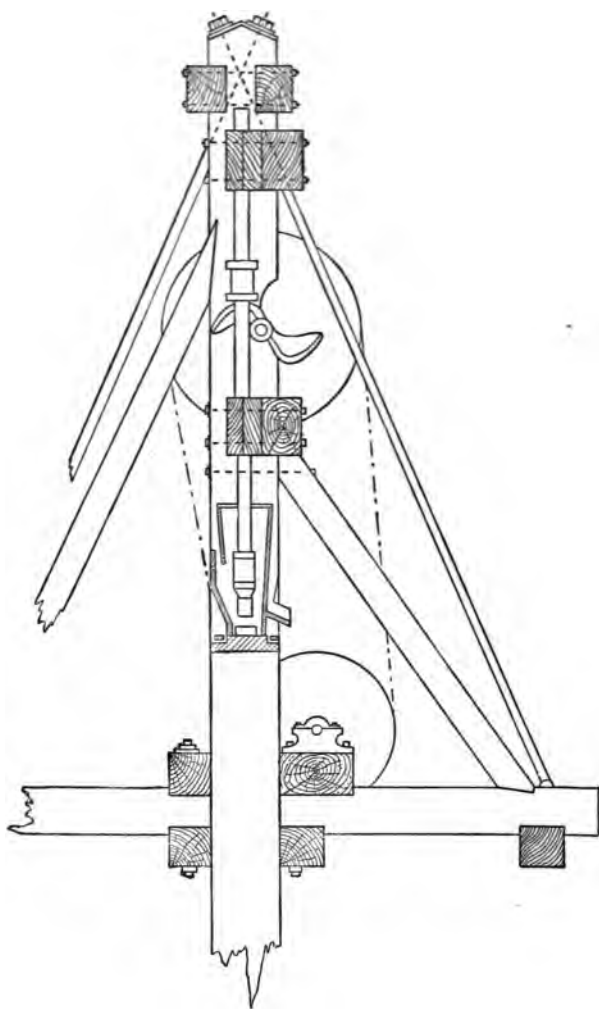
Fig 86.

The amalgamation method is now largely practised for both silver and gold ores in California, Nevada, and other silver producing districts, in iron pans, provided with mullers or grinders, for grinding and amalgamating the ore, either in the raw state or after a preliminary roasting. By this means the silver and its compounds are more effectively brought into contact with chemical reagents and mercury, and the amalgamation is greatly facilitated. Some of these pans, of which there are a considerable number, have false bottoms which allow of admission of steam for heating the pan and its contents. The ore is first broken by rock breakers to small lumps, and then crushed to a powder in stamp batteries, sufficiently fine to pass through a sieve of 30 meshes to the linear inch, fixed on one side of the mortar. The mud passes through this screen directly into settling tanks, or if free gold is present, it is passed over amalgamated copper plates to extract the gold before falling into the settling tanks. The heavier portions containing the precious metals gradually settle to the bottom, and are then collected and transferred to the amalgamating pans.

Fig. 86 shows the stamp in transverse section. It consists of a vertical iron rod or stem, to the bottom of which is attached a larger piece of iron, termed the head, 8 inches in diameter and 15 inches high. At the lower end of the head is fixed a shoe to protect the head ; it is made of the hardest white iron, and so connected as to be removable when worn out. At the upper part of the stem is a projecting piece, termed the tappet, by means of which the stem can be lifted by a revolving cam and then let fall on the die at the bottom of the mortar. The stem is kept in position by wooden guides, one set being placed below the tappet and another set near the top of the stem. The cam is a curved arm fixed to a shaft in front of the stamp, and by the revolution of this shaft the cam is periodically brought in contact with the tappet of the stamp stem, and in another phase of its revolution it is free, so that the stem is lifted at intervals, depending on the speed of the cam. The mortar is placed on a block and secured by bolts. It is an iron vessel, 4 to 5 feet long and the same in depth, and 12 inches wide. On one side is a feed opening, 3 to 4 inches wide and nearly as long as the mortar. On the opposite side is a discharge opening, covered with a screen nearly the length of the mortar, and through which the crushed ore has to pass. The screen is made of fine brass wire cloth, with 40 to 60 meshes to the linear inch, or of sheet iron perforated with very fine holes, which is pre-

ferred for wet crushing (see Fig. 107A). The bottom of the mortar contains the die, which receives the blow of the stamp. It is a cylindrical piece of cast iron, 4 to 6 inches high, corresponding to the shoe of the stem that falls on it.

The Knox Pan.—This pan is very much in use, and is capable of grinding, in three separate charges, the skimmings of a thirty-stamp mill in twenty-four hours. Fig. 87 illustrates this pan in vertical section and plan. It is of cast iron, and is 4 feet in diameter and 14 inches deep. The sides are $\frac{1}{2}$ inch, and the bottom $\frac{3}{4}$ inch thick. The pan is supported

Fig. 87.
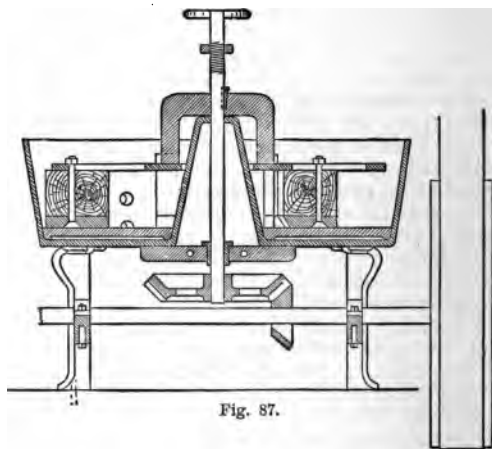
by four cast-iron legs bolted to the floor, and attached to the pan, similar to a stove leg. On the legs are projections which support the cross-bars bearing the driving shaft. The vertical pinion wheel can be put in or out of gear by a bevel clutch worked by lever.

The pan has a false bottom $1\frac{1}{4}$ inches thick, with a projecting vertical rim at the periphery, to form a hollow annular space underneath for the introduction of steam. There is also a radial groove in the false bottom, $1\frac{1}{2}$ inches wide and 1 inch deep, for the accumulation of quicksilver and amalgam, which connects with the lower discharge hole situated opposite the driving shaft. The upper discharge

hole is 4 inches above the lower one.   The holes are closed
by wooden plugs, 2 inches in diameter.

The centre of the yoke attached to the muller is keyed
to a vertical wrought-iron shaft 2 inches in diameter, which
latter is guided by a hollow cast-iron cone in the middle of
the pan.   The muller consists of a flat ring made of cast iron,
having an inside diameter of 10 inches, and being 4½ inches
wide and 1 inch thick.   Attached to the muller are four
arms, 12 inches long and 6 inches wide, placed at right
angles to each other, to which cast-iron shoes, 1½ inches
thick, are bolted.   Between the muller and the iron shoe, a
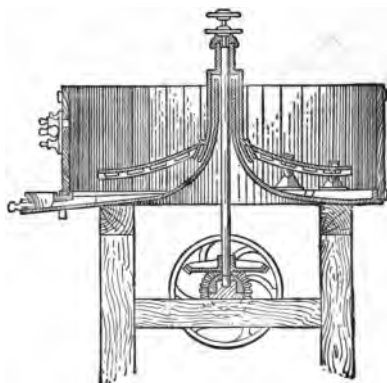
Fig. 88.

wooden shoe, having exactly the same shape as the iron
one, and about 6 inches high, is introduced to prevent the
unground pulp from settling on the latter, the upper face of
the wooden shoe reaching above the surface of the pulp.
The head of the bolt, passing through the shoe and muller
arm, fits into a recess in the bottom of the iron shoe, and
wears off gradually with it.

The yoke, bolted to the muller, serves the purpose of
raising or lowering the latter by means of a screw, which
rests on the vertical driving shaft and passes through the
centre of the pan.   The muller makes from twelve to four-
teen revolutions per minute, the force for which is communi-
cated from the horizontal shaft by bevel gearing, which
makes from thirty to thirty-five revolutions per minute.
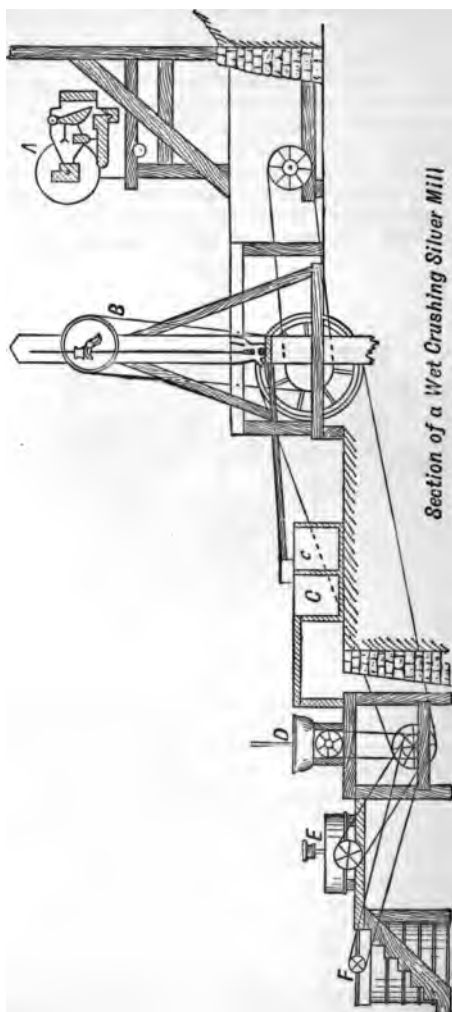
Section of a Wet Crushing Silver Mill

Fig. 89.

The Settler or Separator (Fig. 88).—This is a circular iron vessel somewhat similar to the amalgamating pan, but of larger dimensions, having a hollow cone in the centre, through which passes an upright shaft, made to revolve by gearing below the pan. At the upper end of this shaft is a yoke, and connected to the yoke are arranged horizontal bars carrying a number of vertical stirrers, which usually terminate in wooden blocks just touching the bottom of the pan. By the revolution of the stirrers, the whole muddy contents are kept in motion, with the result that the heavier portions settle towards the bottom and the lighter portions towards the top, and as water is permitted to flow in, these lighter matters are carried away through a discharge hole at the top. The fluid amalgam is finally run off through a hole
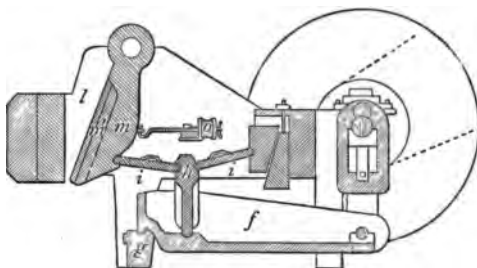
Fig. 90.

near the bottom, which is stopped by a plug during the operation.

Process of Pan Amalgamation.—The arrangement of the various apparatus is shown in Fig. 89. The ore is first roughly crushed by ordinary rock breakers, of which Blake's may be taken as a type (Fig. 90). It consists of a movable jaw m, which is hung on an iron rod and is capable of a small to and fro motion in the direction of a fixed vertical iron block. A lever f rises and falls on a fulcrum at g, and alternately straightens and bends the toggle joints i, i. Each vibration of the oscillating lever causes the lower end of the jaw to advance and then return, thus crushing the material placed in the space l. From the rock breaker the ore is passed to the stamps, which vary in weight from 700 to 1000 lbs., and have a drop of 8 or 9 inches, making eighty or ninety blows per minute. They are arranged in series of four or five, termed a battery.

In wet crushing the ore is fed into the mortars along with a stream of water, which, flowing off through the sieve, carries the finely-crushed ore with it, in the form of a mud, into rectangular tanks, so as to allow the ore to settle, while the water, carrying with it some slime, flows away, and this is often carried into large open ponds to allow it gradually to settle.

The ore from the settling tanks is now fed into the amalgamating pans in charges of 1000 to 2000 lbs. according to the size of the pan. The muller is lifted a little from the bottom so as to revolve freely at first. Water is run in to bring the ore to the consistency of a thick paste. The muller is then lowered and the grinding continued until the material is reduced to a fine flour. The muller is then slightly raised and 50 to 100 lbs. of mercury gradually charged in. The revolving mullers now act as stirrers, and the amalgamation process lasts about two or three hours. If the mullers were allowed to remain in the former position the mercury would be reduced to a powdery condition, termed " flouring," and its final recovery would be difficult. When the amalgamation is complete, water is run in, the mullers raised and kept revolving for some time. The charge is now in the form of a thin mud, and is run off through an orifice, which is now opened in the lower part of the pan, into the settler, which is placed in front of the pan and at a lower level. The charge is then further diluted with water, and the stirrer being set in motion, the mercury and amalgam gradually settle to the bottom. From the settler, the amalgam is conveyed to a vessel where it is washed from dirt by agitating with water, and thence to a strainer where the fluid amalgam is run off from the richer solid, or semi-solid, amalgam and re-treated with fresh ore in the pans. The amalgam left in the strainer is then heated in iron retorts to volatilise the mercury and leave the silver and gold.

The thin mud escaping from the settler is generally conveyed to a large vessel in which are arranged rotating rods or paddles to cause the heavier matters to settle, which are then passed over blankets, or through vanners to collect pyrites and other undecomposed matter containing the precious metals.

It is a common custom to add certain chemical compounds, chiefly copper sulphate and common salt, to the charge in the amalgamating pan with the view of promoting amalgamation. The copper sulphate may assist in forming an amalgamated surface on the iron of the pan and in keeping

the mercury active. Sometimes copper sides are made to the pan in cases where the ores employed are rich in copper, which would rapidly corrode the iron. In this case the ore is first dried and roasted with salt, which involves dry crushing.

Dry Process.—Ores of silver containing much base metal, such as copper, cannot be treated by the former method
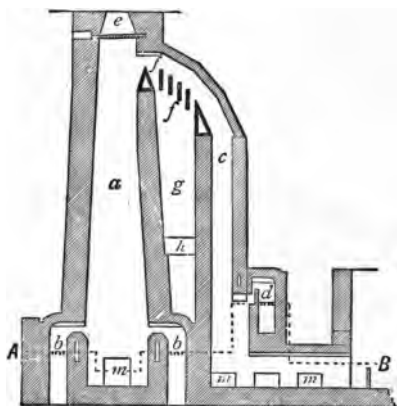
Fig. 91.
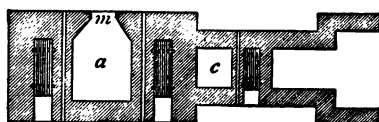
Fig. 92.

of wet treatment, but require to undergo a preliminary roasting in order to remove sulphur, arsenic, etc., as much as possible, and to convert the silver into chloride by means of common salt. If the quantity of base metals is very large, the ore is unfit for the amalgamation process, since metals such as copper and lead are alloyed with the silver at the finish, so that one of the wet methods of extraction is best in this case. Ordinary reverberatory furnaces are now very

little used, but the Stetefeldt and various revolving furnaces are very largely employed.

Stetefeldt Roasting Furnace (Figs. 91, 92).—This is a kind of reverberatory furnace in which the laboratory has been considerably increased in height, and the ore, allowed to fall through an ascending gaseous current produced by the flames from lateral fireplaces, so that the sulphur and other volatile matters are burned off from the ore and in the presence of salt the metals are converted into chlorides. The shaft or laboratory portion *a* varies from 26 to 36 feet in height and 4 to 5 feet square at the base. It is heated by the flames from the lateral fireplaces *b*, *b*. The flue *c*
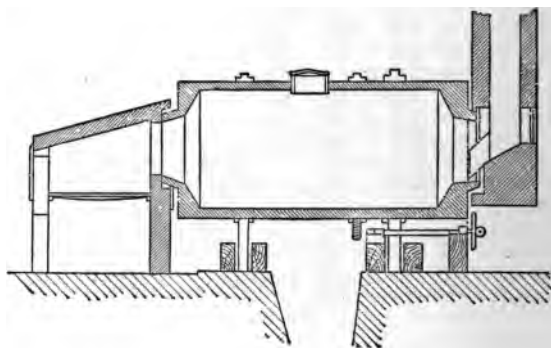
Fig. 93.

is also heated by a separate fire *d*, which helps to complete the roasting, and carries off the waste gases and residual dust. At the top of the shaft is a hopper *e*, which mechanically feeds the powdered ore in a fine stream through a sieve into the furnace. At *f* are fixed iron plates forming a grating through which the dust, mechanically carried over with the gases, can fall into the settling chamber *g* and be removed by the door *h*. The roasted ore is discharged into cars at *m*, *m*, running on a tramway. 60 to 70 tons of ore may be treated daily in this furnace.

Brückner Cylinder (Fig. 93).—This is an iron revolving furnace used for roasting silver and other ores, with or without common salt. The exterior is made of boiler plate and the inside is lined with brickwork. At one end of the

furnace is a fireplace which communicates with the interior by a short flue, and at the opposite end is a brick dust-chamber, which is connected by a flue with the chimney. The roasting chamber or laboratory is a horizontal iron cylinder with conical ends, about 8 feet in diameter and 15 to 20 feet long, and provided with two doors for charging and discharging the ore. It also contains a series of openings, surrounded by frames secured on the outer face of the cylinder and arranged to form internal pockets, which may be opened when necessary. All the pockets of one series nearest one end of cylinder are placed at an incline to the axis of the cylinder, so that the ore elevated thereby may be thrown towards the opposite end; and the pockets at the other end of the cylinder are inclined in an opposite direction. By this means the revolution of the cylinder causes the ore from one or other of these series of pockets to fall through the flame and air, and thus every portion becomes completely roasted. The cylinder rests on friction rollers, and is revolved by means of gearing on the exterior. In some cases the fireplace is arranged on wheels so as to be easily detachable for repairs, etc. The roasted ore, when completed, is discharged into trucks placed beneath. In the presence of the volatile elements—arsenic, antimony, zinc, etc.—the ores must be roasted at low temperatures, or some of the precious metals will be carried off with the volatile metals.

The White-Howell furnace is a cast-iron revolving cylinder lined with brick, 4 to 5 feet in diameter and 27 feet long. It is arranged so as to incline downwards from the feeding end to the fireplace, and as the ore passes over areas of increasing temperature, it is well roasted. As the roasted ore is removed fresh ore is fed in, so that the operations are continuous.

The O'Hara furnace is constructed with two separate hearths forming two steps, one for desulphurising and the other for chlorinising, both being performed in one operation. The furnace is stationary, but mechanical agitation of the ore during roasting is effected by means of an endless chain, carrying, at certain distances apart, triangular iron frames, on which are a number of ploughs or hoes, set on an angle, and by their motion turn over the ore so as to expose every part equally. The furnace is built on the incline. The ore is fed into the upper hearth and the ploughs move it forward to the opening, where it falls into the lower hearth, the heat of the fire being assisted by the combustion of the sulphur of

the ore. Salt is now added and becomes thoroughly mixed with the oxidised ore by means of the ploughs. The total length of the hearths is 120 feet, and total width 8 feet. The furnace is continuous in its action, and will contain a charge up to 50 tons. Some smaller furnaces work with 20 tons.

Ore driers.—Ores for dry crushing are previously dried in various ways, but generally in a revolving iron cylinder heated by a fireplace fixed at one end. The cylinder may be about 40 inches diameter and 18 feet long, and capable of drying 30 to 40 tons at one time.

Dry crushing and roasting reduces the capacity of a silver mill, for a given number of stamps, to one-half the output, and the roasting may lead to loss of metal, as before mentioned, and to the conversion of some of the gold into a soluble form, which is lost in the after pan treatment, but the adoption of the dry or wet treatment is determined by the nature of the ore and other conditions of the locality in which it is used. When dry crushing batteries are employed, the whole of the screens are covered in and the crushed ore conveyed away by belts or screw conveyers. The pans are placed in front of and below the stamps instead of in front of the settling tanks, as in wet crushing mills. The pans are often built with wooden sides on a cast-iron base, as the corrosion of the iron is considerable, the chlorides of lead, silver, and copper being reduced by iron as well as by mercury. A 5-foot pan, 40 inches deep, will treat 1400 to 1500 lbs. The charge is made into a thick paste, and the temperature kept at 80° to 90° C. The operation lasts four to five hours, and the mercury added varies from 200 to 500 lbs. according to the richness of the ore. Copper sulphate and common salt in small quantities are usually added.

CHAPTER XIV.

WET METHODS.

THE methods are based on the principle of converting insoluble silver compounds into a soluble form, and then precipitating the silver by means of another metal, such as copper, or precipitating it in the form of an easily decomposable compound, such as silver sulphide. Three principal methods are employed, viz.—Augustin's, Ziervogel's, and Von Patera's.

Augustin's method.—This was introduced by Augustin for argentiferous copper regulus and various residues containing silver, as well as for argentiferous pyrites and similar ores, but it is now seldom used for ores, and chiefly confined to the former class of substances. The substance is first reduced to a very fine state of division by means of stamps or rollers, and then roasted in a reverberatory furnace, at a moderate temperature and with frequent stirring, to remove excess of sulphur, which passes off as sulphur dioxide, SO_2; the heat is now gradually raised, when the sulphates of iron and copper are decomposed, with the evolution of sulphur trioxide SO_3 in the form of white fumes, leaving the above metals in the form of oxides. The substance is then said to be roasted "sweet." It is raked from the furnace, allowed to cool, and again ground to a fine powder between rolls, as the mass cakes together somewhat during the roasting. It is then transferred to the furnace, mixed with 5 per cent. of common salt, and the whole roasted for two or three hours with frequent stirring, when the silver is gradually converted into silver chloride.

The roasted product is next placed in wooden vats (Figs. 94, 95), having false bottoms, on which are placed twigs and straw, the whole being covered with a stretched

linen cloth to act as a filter. These vats are arranged in tiers. The top row receives the roasted material, and on to it is run a hot and nearly saturated solution of common salt to dissolve out the silver chloride. This is termed "lixiviation." The solid material being hot when charged into the vats, the brine acts vigorously on it, and the solution containing the silver filters through the false bottom, and may be drawn off by a suitable tap into the next row of vats below marked B, which act as settlers for any suspended matter. The clear liquid is run out of these into the next and lower series, marked C, which have false bottoms like the first, but they contain a layer of cement copper 6 inches thick, which precipitates the silver, as shown in the equation :

$$Cu + 2AgCl = CuCl_2 + 2Ag.$$
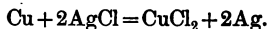
Thus the copper combines with the chlorine from the silver chloride and passes into solution, leaving the silver in the metallic state. This copper solution is then run off into D,
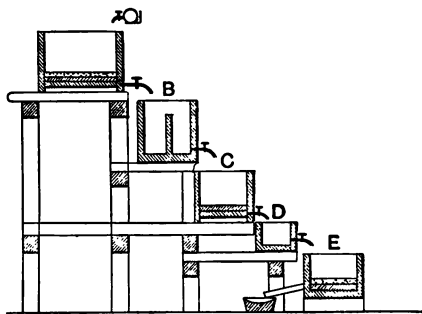
Fig. 94.
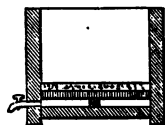
Fig. 95.

where any undecomposed silver chloride is completely reduced and precipitated. Lastly the copper solution is run into a still lower series of tubs (E), when the copper in solution is recovered by precipitation with scrap iron, thus :

$$CuCl_2 + Fe = FeCl_2 + Cu.$$
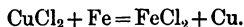
The precipitated silver is collected and treated with hydrochloric acid to dissolve out any copper, and then refined.

Ziervogel's method consists of roasting finely powdered

ore, containing silver sulphide in admixture with copper pyrites, to silver sulphate, dissolving the sulphate in water, and precipitating the silver with copper. The perfection of the process depends on the preliminary roasting and the amount of copper and iron sulphides present. At Mansfeld, where the method was introduced, the ore contains about 80 per cent. Cu_2S, 11 per cent. FeS_2, and 0·4 per cent. of Ag_2S. The iron and copper sulphides are decomposed, liberating sulphur trioxide, which in turn converts the silver sulphide Ag_2S into silver sulphate Ag_2SO_4. In many places where this method is employed the ores to be treated contain very little copper, but several ounces of silver and varying amounts of gold to the ton. Such ores are treated as copper ores by alternate roastings and meltings so as to produce a coarse regulus, or they are smelted direct with copper regulus, in order to concentrate the precious metals. The regulus containing the gold and silver is smelted with siliceous substances to slag off iron and other impurities, and the enriched regulus, corresponding to "blue metal," is then subjected to the Ziervogel process. The roughly crushed material is first roasted to remove excess of sulphur, then removed, allowed to cool, crushed to a very fine powder, and roasted at a low temperature for about one and a half hours, when any iron is converted to sulphate; the temperature is then raised and the roasting continued for a similar period to convert the copper into sulphate; the iron sulphate is also decomposed. The temperature is again raised, when the copper sulphate is largely converted into oxide and the silver into sulphate. If much lead or antimony sulphide is present a caking of the mass occurs, and the operation is very imperfect. The presence of zinc, arsenic, and antimony in the ore is said to cause loss of silver by volatilisation ; also in the case of arsenic, arseniates are formed, which are very difficult to decompose. The roasting process may be performed in a single or in a double-bedded reverberatory furnace. In the latter case the ore is placed on the top bed for a preliminary roasting, then raked on to the lower and hotter one to finish, with frequent stirring during the roasting. The operation requires about five and a half hours. When the roasting is complete, a portion treated with water should produce a light blue liquid, and a solution of common salt added to this liquid should give a dense precipitate of silver chloride. If the silver and copper sulphates have been overheated, they will be reduced to metallic silver and oxide of copper, and, when this action is complete, a colourless

Fig. 96.
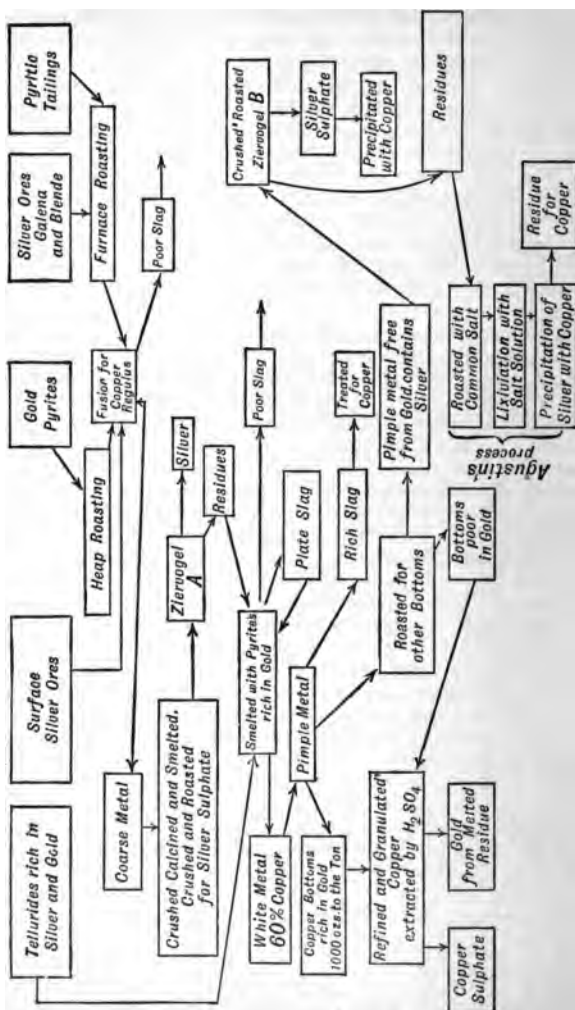
liquid will be obtained by digesting a portion with water. The roasted mass is raked out, allowed to cool, and put into the lixiviating vats at about 90° C., each vat holding about 5 cwts. of material. The structure and arrangement of the vats are the same as in Augustin's method. Hot water is added, which dissolves the silver sulphate. The liquid is filtered, run into the settling tanks, and thence into the precipitating tanks, where the silver is precipitated by copper as before.

The residues from the above method are often rich in silver, due to imperfect conversion in the roasting and to the formation of insoluble compounds, such as arseniates, etc. Gold is also often present. Such residues may be smelted with copper pyrites for the production of a rich regulus and the formation of "copper bottoms" rich in gold and silver. The residual regulus is then treated for the contained silver by the Ziervogel process.

The annexed scheme (Fig. 96) will illustrate the method of extracting silver and gold by a combination of the Augustin, Ziervogel, and copper-bottom methods; the copper being also extracted in the form of sulphate. It also shows the method of extracting metallic copper from certain complex and mixed ores containing tellurides.

1. Tellurides rich in gold are smelted with pyrites rich in gold and residues from the Ziervogel process for the production of a copper regulus, which is afterwards concentrated to blue metal and then to white or pimple metal. From this pimple metal copper bottoms rich in gold are produced. These are refined, granulated and treated with sulphuric acid for the formation of copper sulphate, which is crystallised out, leaving gold in the residual mud.

2. Various ores containing small quantities of silver and gold, together with copper, iron, lead, zinc, etc., are smelted for regulus after a preliminary roasting. This coarse regulus is concentrated to a rich regulus and then roasted for silver sulphate (Ziervogel A), and from this some silver is obtained. The residues from this treatment contain the gold and some silver ; they are smelted with pyrites for regulus and copper bottoms as described in No. 1. The bottoms are treated for the gold, and the regulus is again roasted for other bottoms, leaving a regulus of pimple metal free from gold but containing silver. This is roasted for silver sulphate as usual (Ziervogel B), and the silver in the residues from this process is finally extracted by Augustin's

method of roasting with common salt, dissolving in hot brine, and precipitating with copper.

Von Patera method.—Dr. Percy, in 1848, showed that silver chloride was soluble in sodium thiosulphate, and Von Patera adopted this principle for extracting silver from the rich ores of the Joachimsthal district. The operations consist of : (1) Roasting with common salt to form silver chloride ; (2) lixiviation of the roasted mass in a solution of sodium thiosulphate ; (3) precipitation of the metal as silver sulphide by means of sodium sulphide ; (4) reduction of the sulphide by heat and refining of the silver. This method had a very limited application until Mr. Russel introduced his improvements, which enable much more of the silver contained in the ore to be extracted than in the original process. A further modification was made by Kiss, in which calcium thiosulphate is used instead of the sodium salt, and calcium sulphide as the precipitating agent in place of sodium sulphide. If lead and copper are present in the ore, these metals very largely pass into solution with the silver, and are precipitated simultaneously with the silver sulphide.

Russell * discovered that lead can be precipitated from the solution by means of sodium carbonate, leaving the silver and copper in solution, from which they are precipitated by means of sodium sulphide. He also observed that a solution of the double thiosulphate of copper and sodium (formed by mixing sodium thiosulphate with copper sulphate), exerts an energetic decomposing and dissolving action on metallic silver, silver sulphide, and the combinations of silver with antimony and arsenic. Hence, if the roasted ore is first treated with sodium thiosulphate to dissolve the silver chloride, and the residues subsequently treated with copper thiosulphate solution, much more of the silver is extracted than by the old method, which requires perfect chlorination for success. The reactions are as follows :

$$11Na_2S_2O_3 + 6CuSO_4 =$$
$$2Na_2S_2O_3,\ 3Cu_2S_2O_3 + 6Na_2SO_4 + 3Na_2S_4O_6.$$

$$2Na_2S_2O_3,\ 3Cu_2S_2O_3 + 3Ag_2S = 2Na_2S_2O_3,\ 3Ag_2S_2O_3 + 3Cu_2S.$$
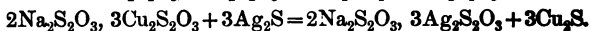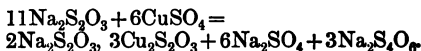
Thus the silver passes into solution and the copper is precipitated, so that the silver may be afterwards obtained nearly free from copper. The double copper-sodium salt is easily decomposed in air, so that it is generally made as required.

* See Eissler's *Silver*, p. 281; also *Dict. of App. Chem.* (Thorpe), Vol. III., p. 305.

The ore is generally roasted in a revolving furnace of the Brückner type, after being crushed to a fine powder in stamp batteries. About 6 per cent. of common salt is used, and sometimes as much as 10 per cent. when a large quantity of base metals are present, but in such a case this method is not the most suitable one to employ. The time required for roasting varies with the nature of the ore from six to twelve hours, and the success of the operation depends on the proper regulation of the temperature, which should be just sufficient to produce a slight clotting of the charge. The contents are then raked out and allowed to cool, during which the chlorinising action continues.

The lixiviation tanks are circular, each being about 14 feet in diameter and 3½ feet deep. The solution is filtered off through the false bottom (see Fig. 95) and run into the precipitating tanks, and the silver sulphide is precipitated as described above. This precipitate is filtered, dried, and then roasted on the bed of a reverberatory furnace at a low temperature, and, if rich in silver, is finally melted in a crucible ; but if poor, it is treated with lead and cupelled.

LEAD METHODS.

These methods are based upon the reducing action which lead exerts on gold and silver ores with the subsequent solution of the metals in the excess of metallic lead, and the final separation of the silver by cupellation.

At Freiberg in Saxony this method is carried out with ores consisting chiefly of argentiferous and auriferous sulphides of lead. As other ores are also treated at these works, the extraction of metals other than those of gold and silver will be incidentally referred to here, and the general system employed may be conveniently explained by reference to the accompanying scheme (Fig. 97).

The principal furnace is known as the Pilz (Fig. 98). The ores are first roasted in a long bedded reverberatory furnace in order to expel much of the sulphur as sulphur dioxide (which is utilised for making sulphuric acid), to convert the mass largely into oxide, and finally to cause the powdered material to cinter or cake together, in which state it is better adapted for blast furnace treatment. It is then smelted in the Pilz furnace, using cold blast so as to prevent too much of the iron present from being reduced. The charge for this operation is made from a mixture of about 450 cwts. of
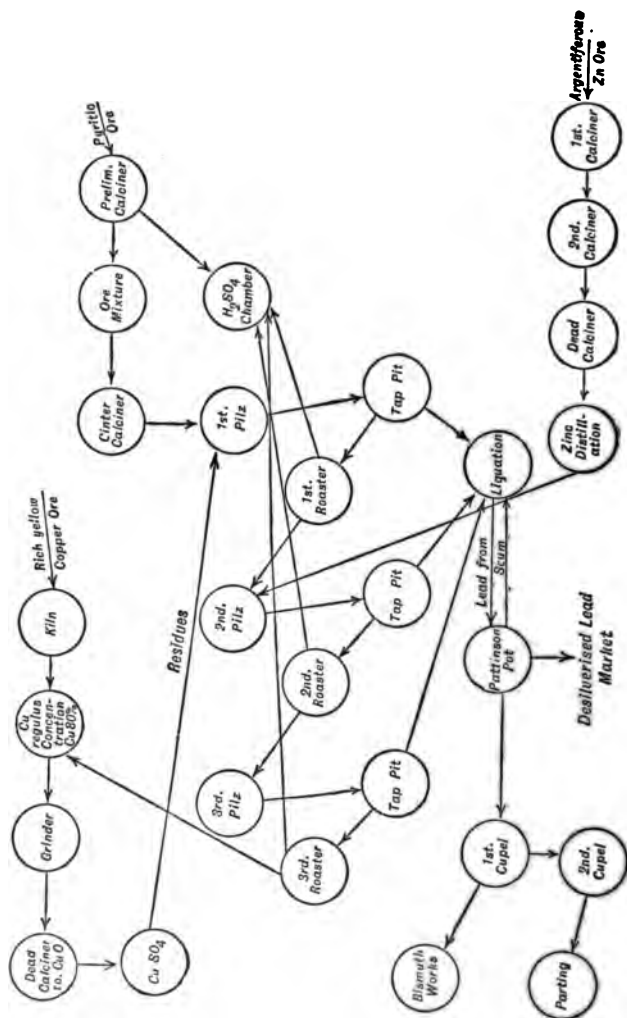
Fig. 97.

roasted ore, 80 cwts. of pyritic ore, 40 cwts. of residues, 550 cwts. of slag from a previous charge, and 20 cwts. of quartzose ore ; yielding 88 cwts. of argentiferous lead, 20 cwts. of regulus, and often some speise containing nickel and cobalt. The pressure of the blast is about 12 inches of water for ore, and about 9 inches of water when smelting slag. The amount of ore treated in twenty-four hours is 1400 to 1500 cwts. The Pilz furnace is a circular shaft of iron lined with firebrick, but the sides of the furnace, in the region of fusion, are constructed of cast-iron boxes through which water flows to keep the temperature down. The bottom is also lined with firebrick, and on this is melted a layer of slag. There are four tap-holes and two slag lips. The blast is supplied through eight twyers. The throat is closed, except while charging, by a cylinder, and the waste gases are carried off by a side pipe.

Fig. 98.

The products from the above furnace are: (1) impure lead, containing most of the silver and gold ; (2) regulus, chiefly sulphides of copper and lead ; (3) slag, consisting of various silicates ; (4) lead fume. Sometimes a speise of nickel and cobalt is obtained. The slag from ore smelting is again smelted with materials poor in silver and lead, when similar products to the above are obtained, but the lead is of much inferior quality ; speise is a less frequent product ; the regulus is richer in copper and the slag is sufficiently poor to be thrown away.

The regulus is roasted and smelted with another charge in the Pilz blast furnace No. 2, producing as before, lead, regulus, and slag. The same cycle of operations is again repeated, and the regulus smelted in the Pilz No. 3, and the regulus now obtained is sufficiently rich in copper and
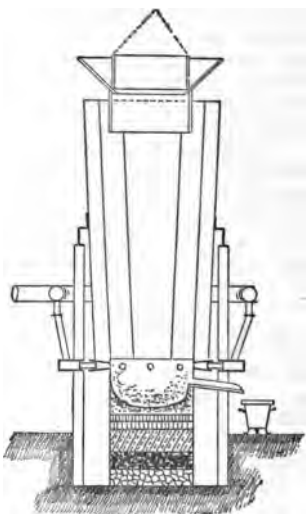
sufficiently free from lead to be treated for the production of copper or copper sulphate.

The different portions of lead obtained by the above successive smeltings are very impure, but contain nearly all the gold and silver originally present in the ore. The lead is submitted successively to liquation, pattinsonisation, cupellation, and parting, all of which will be subsequently described.

Ores of zinc containing silver are roasted in reverberatory furnaces, the sulphur dioxide being conveyed to the sulphuric acid chambers, and the oxide of zinc produced is reduced by carbon in closed retorts, when the liberated zinc distils over into suitable condensers. The residues left in the retorts contain the silver and are smelted in the Pilz furnaces with lead ores.

The speise, which is occasionally produced, is treated by a series of roastings and smeltings with lead slags, so as to gradually concentrate the nickel along with arsenic while the slags remove other metals, and the reduced lead will contain any gold and silver that may be present. The nickel speise is then sold to nickel smelters.

If any bismuth is present in the original ores, it will keep in company with the lead. When the lead-bismuth alloy is cupelled, the lead will be largely oxidised and removed first, and where the final alloy—rich in gold and silver—collects, the bismuth will be oxidised and show a green stain after the gold and silver are removed. This portion of the bed is carefully removed and the bismuth extracted by the ordinary chemical method of solution and precipitation as oxychloride, which may be reduced in crucibles.

For the treatment of lead fume, see Lead, p. 286.

LIQUATION.

The liquation process has been employed from remote times to separate silver from argentiferous copper by dissolving it in molten lead, but the method is now little used. It consists of three processes : (1) alloying with lead ; (2) liquation proper; (3) treatment of the residual copper and liquated lead. The following may be taken as a typical case:

1. 100 lbs. of crude copper containing about 2 ounces of silver is melted with 250 lbs. of lead, and poured into a casting pan 2 feet in diameter and $3\frac{1}{2}$ inches thick, forming a circular cake.

2. A number of these cakes having been cast, they are placed on the liquation hearth (Fig. 99), which consists of two walls, covered with iron plates, inclining towards a median line, leaving a space of 2 to 3 inches through which the liquated metal drops and runs along a gutter into a basin outside. The cakes are surrounded by an iron frame, and packed round with charcoal to exclude air. A wood fire is then lighted underneath and the temperature regulated by a damper in the back wall. In about an hour the lead begins to liquate out, carrying the silver with it ; when the flow ceases, the fire is allowed to die out. The residual copper contains about one-third its weight of lead, with some silver ; the liquated lead contains 2 to 3 per cent. of copper and most of the silver.
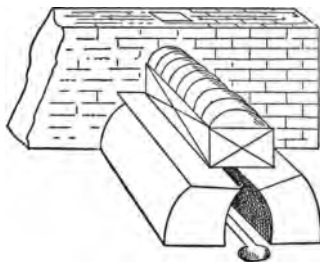
Fig. 99.

3. The residual copper, containing lead and silver, is exposed to a prolonged high temperature in a hearth furnace, provided with a twyer, by which means the lead and some copper are oxidised, leaving an impure copper which is afterwards refined. The liquated lead is treated by cupellation for the recovery of the silver.

Fig. 100.

Extraction of Silver from Lead.—Mr. Pattinson, in 1833, discovered that when argentiferous lead is melted and allowed to cool slowly, and constantly stirred, the lead separates out in crystals at its solidifying point, leaving a molten mass of lead very much richer in silver than at first. Thus lead, containing only 3 or 4 ounces of silver to the ton, can be profitably treated for the extraction of the silver.

Pattinson's process is conducted in a series of 9 to 15 cast-iron pots (Fig. 100), each capable of holding from 3 to 8 tons of lead, and sometimes as much as 15 tons, heated by a separate fire. Suppose 3 tons of lead, containing 10 ounces of silver per ton, is first melted in the middle pot of the series, say No. 8, it is then well stirred, skimmed, and allowed to cool, or water is sprinkled on ; at a certain temperature the poor lead separates in crystals, which are removed as they form by a perforated ladle and transferred to the next pot on the right, No. 9, leaving a rich liquid argentiferous lead in the pot, which, when the operation has been carried sufficiently far, is conveyed to the next pot on the left, No. 7. This will contain 1 ton of the enriched lead, while No. 9 will contain 2 tons of the impoverished lead. Each pot is then made up to 3 tons with lead, containing the same amount of silver as that transferred to the respective pots, so that the same quantity of metal is operated upon in each case. The operation of melting, skimming, and cooling, with constant stirring, is repeated in Nos. 9 and 7, when the lead is further enriched in the latter and impoverished in the former, so that when the portion travelling to the right reaches No. 15 pot it is nearly free from silver, while, when the portion, which is transferred in the opposite direction, reaches No. 1, it probably contains 250 ounces of silver per ton ; but it may be concentrated to contain 700 ounces, beyond which it is not practicable to go.

The method of thirds described above is known as the high system ; but sometimes 8 tons are treated in each pot, and 7 tons of crystals skimmed off: this is termed the low system. At each melting a certain amount of oxide or dross is formed which is kept for future reduction. This repeated oxidation greatly purifies the lead and increases its value for commercial purposes.

Rozan method.—In this process superheated steam is forced into the molten lead, and by its mechanical agitation favours the production of crystals poor in silver ; it also acts chemically in promoting the oxidation of impurities. The pot A (Fig. 101) is simply for melting the lead, which is then run into the crystallising pot B, and steam distributed by means of a baffle plate C. A spray of water is allowed to play on the surface of the metal to assist in cooling it. When the crystallisation has proceeded sufficiently far, the liquid alloy is run off, leaving the crystals in the pot. The operation is then repeated till the lead is sufficiently enriched.

Parkes' process, introduced in 1850, depends on the principle that, when lead containing zinc and silver is melted and allowed to cool, an alloy of zinc and lead crystallises at a certain temperature and contains nearly all the silver. The argentiferous lead is melted in an iron pot, raised to above the melting point of zinc, skimmed, $1\frac{1}{2}$ to 2 per cent. of molten zinc added, and the whole constantly stirred, while the temperature is gradually lowered until the zinc separates as a crust on the surface. These crusts, containing silver and some lead, are removed until an assay shows that the remaining lead is sufficiently low in silver : they are next
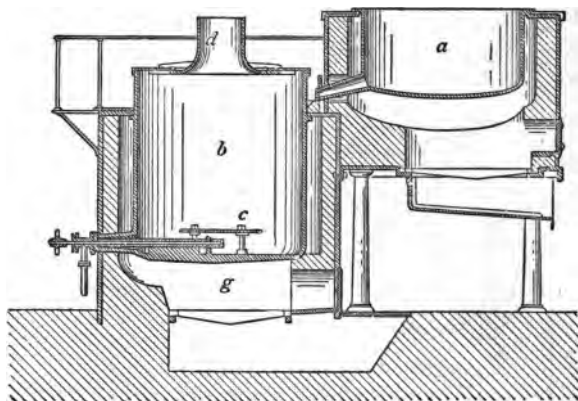
Fig. 101.

heated to a little above the melting point of lead in a cylindrical retort open at the front, and inclining from back to front, when the lead liquates out, carrying much of the silver and a little zinc with it. The unmelted residue is then heated with lime and coal in a closed retort by which means the zinc is distilled, leaving a mass of silver, lead, copper, etc., behind. The rich lead obtained by Parkes' or Pattinson's methods is treated by cupellation for the separation of the silver.

The desilverising of lead is said to be facilitated by passing a voltaic current by means of copper wires through the lead after adding the zinc, until all the zinc has risen to the surface.

The difficulties in the way of a successful application of the process are : (1) The contamination of lead with zinc, and the loss of silver in removing it from the zinc-lead alloy.

Cordurié improved on the original Parkes' process by employing two vessels, as shown in Fig. 102. The lead is melted in the cast-iron pot *a*, and the zinc introduced by a perforated box *b*. At the same time a rapid motion is given to the rod, which also carries a stirrer *c*. The zinc is thus distributed through the lead by centrifugal action, and when the crystallisation has proceeded sufficiently far, the
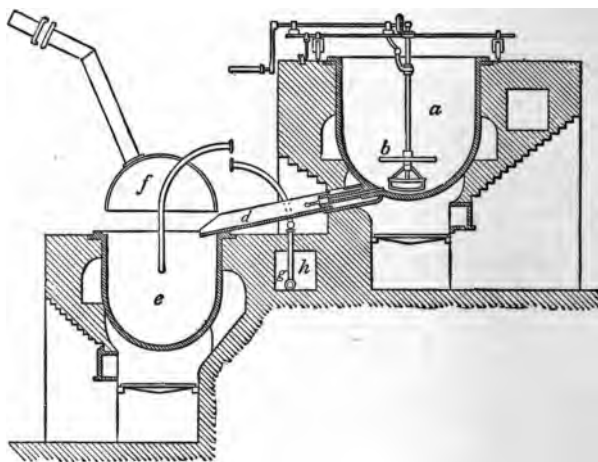
Fig, 102.

paddle is removed and the desilverised lead run into the pot *e*, heated by a separate fire. This vessel is fitted with a lid. Steam is introduced by the pipe *f*, and is said to oxidise the zinc and bring it to the surface. Any volatile matter is carried off by the exhaust pipe *h*.

Cupellation.—This is a method for the separation of base metals as oxides, in conjunction with oxide of lead, from silver and gold, which do not oxidise. Two methods are employed, known respectively as the German and the English. The German hearth (Fig. 103) is of the reverberatory type, but without a chimney, the volatile products

escaping through an opening opposite the bridge. The bed, which is circular and concave and about 10 feet in diameter, is made of marl, which is chiefly composed of carbonate of lime, carbonate of magnesia, and clay ; the roof is formed of a movable iron cover lined with clay ; the air is supplied by a pair of inclined twyers fixed in one side of the bed, and the oxide of lead flows off through an opening opposite the twyers. When the lead is melted by means of a wood or coal fire, the blast is continued until the surface brightens, showing that the silver is comparatively pure and free from oxide. It then contains 90 to 95 per cent. of silver, and is refined on a bed of bone ash. Water is then thrown on the fire and on to the bath of silver, which soon solidifies. The silver thus obtained is further purified by melting in a small reverberatory furnace similar to the above, or in a plumbago
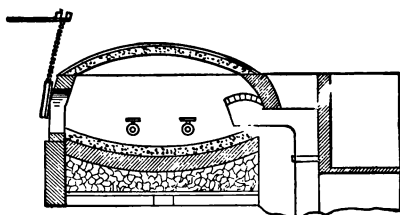
Fig. 103.

crucible. The charge of argentiferous lead is melted in three or four hours, and the metal has a layer of dross, consisting of oxides of lead and other base metals, which is dark in colour, and termed "Abzug." This is raked off, and the dross which subsequently forms is purer and more fluid, termed "Abstrich." This is also raked off, when the remaining oxide formed during the cupellation is nearly pure litharge. The cupellation of 10 to 15 tons of lead requires 70 to 80 hours.

The English process is conducted in a reverberatory type of furnace (Fig. 104) with a movable bed, called a "test," made of bone ash. An oval frame of wrought iron, about 5 feet long and 3 feet wide, is well lined with moistened bone ash mixed with a little pearl ash, 1 inch thick, leaving a cavity which inclines from the sides to the centre, on which the metal is afterwards melted and refined (Fig. 105). The breast of this test is perforated with a number of holes for

the removal of litharge as it forms.   Some tests are kept
in stock, as several weeks are required to gradually and
thoroughly dry them after making.   Bone ash differs from
marl in that it absorbs a considerable portion of the litharge
formed during cupellation.   The test having been raised to
a red heat, the argentiferous lead is charged in and melted.
At first a grey dross forms, and afterwards litharge.   The
blast is now turned on, when most of the litharge as it forms
is blown to the opposite side and overflows into an iron pot
below.   Fresh lead is added as the oxidation proceeds, and
when large quantities have to be cupelled, the operation is
conducted until the lead contains about 10 per cent. of silver,
when it is tapped off through a hole made in the bottom of
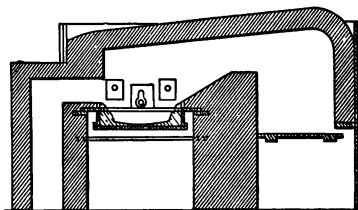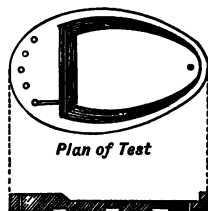
Fig. 104.   Fig. 105.

the test, and completed in a second cupel.   Sometimes the
cake of silver is allowed to cool in the furnace and detached
when cold.   The silver obtained is practically pure, and one
cake may weigh 10,000 to 20,000 ounces.

SILVERING.

This is the art of covering articles with a coating of silver,
either in the form of leaf and sheet or by electro-plating.
In the former method the base metal to receive the silver is
made perfectly smooth, and then thoroughly cleaned by dip-
ping in acids, and finally well swilling in water.   The metal
is then slightly warmed, and dipped in aquafortis to produce
a slight roughness.   The next operation is to make the metal
hot, and placing the leaf on the hot surface, to fix it by well
rubbing with steel burnishers.   This operation is repeated
until a number of leaves have been fixed one on the other,
according to the thickness of the plating required, and finally
well burnishing to produce a compact and uniform surface.

This is the French method. In England sheet silver of the desired thickness is soldered on to a previously tinned surface by a soldering iron and afterwards burnished.

Electro Deposition.—Silver is very extensively used for coating base metals by electroplating, the best solution for that purpose being the double cyanide of silver and potassium, which may be obtained either by the chemical or by the battery method.

1. *Chemical method.*—Dissolve 2 ounces of fine silver in dilute nitric acid ; evaporate to dryness on a sand bath ; re-dissolve in water, and add a strong solution of potassium cyanide, stirring all the time until the whole of the silver is precipitated ; allow to settle ; pour off the clear liquid and again add potassium cyanide until the precipitate just re-dissolves ; now add one-fourth more to form the free cyanide, and make up the solution to one gallon.
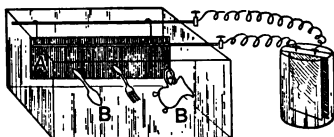
Fig. 106.

Battery method.—Make a solution of potassium cyanide containing 1½ ounces to the gallon ; suspend a large silver anode and small silver cathode in the solution, then send a current through the liquid until a piece of bright and clean brass receives a good deposit.

Fig. 106 represents a silver plating vat with a copper-zinc battery attached. The silver plate (A) is connected with the positive (+) or copper plate of battery, and is called the "anode," or the part where the current enters the liquid ; the article (B) to receive the deposit is connected with the zinc or negative (−) plate of the battery, and is called the "cathode," or the part where the current leaves the liquid.

The work to receive a deposit must be scrupulously clean, for which purpose it is generally boiled in a solution of potash to remove grease, then well swilled in clean water. In the case of copper, brass, or German silver, the cleaned articles are dipped in a solution of mercury, in order to cover the surface with a film of that metal, which greatly

aids in the perfect deposition of the silver. Articles of zinc and iron are generally coated with a thin film of copper, in a copper cyanide solution, before immersing in the silver bath. Articles of tin, pewter, and Britannia metal are taken from the potash solution to the silver solution without swilling in water ; but for these metals a special silver solution is generally kept.

Silver may be stripped from old plated articles without affecting the base metal, by using a mixture of 3 lbs. of sulphuric acid diluted with 1 lb. of water and 1½ ounces of nitre.

CHAPTER XV.

GOLD.

GOLD has been known from the earliest times and, in consequence of its rarity and valuable properties, has been esteemed the most valuable of metals. The search for gold, and the endeavour to obtain it by the transmutation of base metals, has led to many important discoveries, and the study of its properties in early times greatly assisted in laying the foundations of the modern science of chemistry. The dreams of the old alchemists have not been fulfilled, but the results of their earnest endeavours have been handed down to succeeding generations as a rich legacy of far greater value than perhaps we are willing to admit. The search for gold in various substances led also to the study of the metallurgy of lead, copper, and other metals, as well as to the investigation of various fluxes and re-agents which are indispensable to the metallurgist of the present day. The ancients were well acquainted with the action of lead and mercury in extracting gold, and the principles they adopted as regards cupellation and amalgamation are those now largely used. Gold, therefore, not only by its own intrinsic value, but by the researches to which it has given birth, is entitled to be justly ranked as one of the most valuable of metals.

In the pure state, and in mass, it has a yellow colour, but in a finely divided condition, such as the precipitates obtained by adding various re-agents to gold solutions, or by volatilisation at high temperatures, it may have a violet, ruby, purple, or brown colour. When in thin leaf, and viewed by transmitted light, it has a green colour. Molten gold has a greenish tint, and its vapour has a similar colour. Its lustre is proverbial, and this is enhanced by the fact that it undergoes very little change by prolonged exposure to the atmosphere. It exceeds all other metals in malleability and

ductility, and the extreme tenuity to which a piece of gold can be reduced is simply marvellous. It is stated that one grain can be beaten into a leaf $\frac{1}{250000}$ of an inch thick; or can be drawn into wire 160 yards long. It has a tensile strength of 7 tons per square inch, and elongates 30 per cent., when stretched, before breaking. The tenacity of gold is little affected by small quantities of silver, zinc, and cadmium; copper and aluminium increase its tenacity; lead, tin, antimony, and especially sodium and potassium diminish its tenacity, even when present in very small quantities. Most impurities, even in small quantities, diminish its ductility, but copper and silver increase it, the former to a considerable degree. Most impurities harden gold. The specific gravity of gold varies with its physical condition; when cast it is 19·3, and after compression, 19·48. Louis has shown that gold, after parting from silver by the action of nitric acid, has a specific gravity of 20·3. Gold can be welded at a high temperature like iron. Its melting point is 1045° C., and its specific heat is ·032. It has a coefficient of linear expansion of ·0000144 between 0° and 100° C. Its electric conductivity is 77, silver being 100; its thermal conductivity is much less. The boiling point of gold is very high, but it can be somewhat volatilised at much lower temperatures. It is volatile when a discharge from a Leyden jar is sent through a gold wire; and molten gold may be readily vaporised in a strong blast of air, or in the presence of readily volatile elements. Carbonic oxide favours the volatilisation of molten gold.* Gold crystallises in the cubic system, but well-defined cubes, octahedra, etc., are rarely met with.

Gold is not acted on by oxygen or sulphur, either at the ordinary temperature or when in the molten state, but double sulphides of gold and alkali metals may be formed by fusing gold with an alkaline sulphide. Metallic gold is not acted on by sulphuretted hydrogen; but it is precipitated from its acid solution as sulphide by this gas. Gold readily unites with chlorine, forming gold chloride, and it is dissolved by any substance which liberates chlorine, hence its dissolution by aqua regia. The chloride is easily decomposed by heat, and when in solution, by weak voltaic currents. The metal is precipitated by organic substances, such as oxalic acid; by most metals, such as zinc and iron; by metallic salts, such as ferrous sulphate; and by several gases, such as sulphur

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* *Metall. of Gold*, by Rose, p. 6.

dioxide, arseniuretted hydrogen, etc. The following equations will illustrate some of these :

$$2 \text{ AuCl}_3 + 3 \text{ SO}_2 + 6 \text{ H}_2\text{O} = 2 \text{ Au} + 6 \text{ HCl} + 3 \text{ H}_2\text{SO}_4$$
$$2 \text{ AuCl}_3 + 6 \text{ FeSO}_4 \qquad = 2 \text{ Au} + 2 \text{ Fe}_2(\text{SO}_4)_3 + \text{Fe}_2\text{Cl}_6.$$
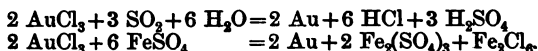
Stannous chloride forms a very delicate test for gold in solution, giving a brown precipitate, or if the gold is exceedingly minute, a violet colour is imparted to the solution. If the re-agent also contains stannic chloride, "purple of Cassius" is precipitated, containing tin oxide and metallic gold. Bromine unites with gold, forming gold bromide, which is very similar in properties to the chloride.

Gold and cyanogen unite in two proportions, forming aurous and auric cyanides. The former AuCy is obtained by heating the double cyanide of potassium and gold (KCy, AuCy) in hydrochloric acid. It is a yellow crystalline powder, insoluble in water, but soluble in ammonia, potassium cyanide, and sodium thiosulphate. It is decomposed by heat. The double aurocyanide mentioned above is prepared by dissolving gold cyanide in a solution of potassium cyanide. This forms the ordinary gilding solution.

Thiosulphate of gold $\text{Au}_2\text{S}_2\text{O}_3$ is of metallurgical importance, being employed in combination with sodium thiosulphate for the extraction of gold and silver from certain ores by the Von Patera method, as improved by Russell. The formula of the double salt is $(\text{Au}_2\text{S}_2\text{O}_3, 3\text{Na}_2\text{S}_2\text{O}_3) + 4\text{H}_2\text{O}$. On the addition of an acid, and with the aid of heat, gold sulphide is precipitated. Russell discovered that gold sulphide was very soluble in the double thiosulphates of copper and sodium $(4\text{Na}_2\text{S}_2\text{O}_3, 3\text{Cu}_2\text{S}_2\text{O}_3)$ in the proportions represented by the above equation. Free gold is also, to a very limited extent, soluble in sodium thiosulphate, and the action is attributed to the oxidation of the gold by the air present in the solution.

Gold exists in some silicates : the ruby colour imparted to glass by gold is well known. If gold chloride, sand, and alkalies or lead are fused together, a yellow transparent silicate of gold is formed. This is decomposed by heat, with the production of free gold. Gold quartz may have been formed in a similar way.

Ores of Gold.—These consist chiefly of quartz, and occasionally of slate, baryta, and talc. Pyrites often contains gold. It occurs in veins and in alluvial deposits. Gold also frequently accompanies silver in various ores of other metals, especially those of lead. It is somewhat widely dis-

tributed over the earth, but generally in very minute quantities in any one place. Alluvial deposits consist of sand from ancient and modern streams which contain gold in the form of minute scales, but occasionally larger and rounded pieces occur. The rounded-off angles are characteristic of alluvial gold, and nuggets have been found of considerable size, one of which, in Victoria, weighed 183 lbs., and was valued at £8,376 10s. 6d. Other minerals occur with native gold, such as platinum, osm-iridium, magnetite, pyrites, galena, blende, garnet, zircon, and barytes, and sometimes diamonds, as in Brazil. Gold occurs also with tellurium in Colorado and Transylvania. The following formula represents some of these : $AuTe_2$ and $AuAgTe_3$. In the latter locality a lead grey ore occurs, containing 32·2 per cent. tellurium, 54 per cent. lead, 9 to 13 per cent. gold, with silver, copper, and sulphur, termed Nagyagite. Gold amalgams are also known. Native gold is found in Australia, South Africa, various parts of America, north and south, in Siberia, in Russia, in Hungary, in Wales, chiefly near Dolgelly, in Scotland, in Wicklow, Ireland, and in India.

METHODS OF OBTAINING GOLD.

Gold Washing.—This method is used for extracting gold from alluvial deposits. Such as occur near the surface are treated in various kinds of apparatus, according to the locality. A shallow pan, made of sheet iron, and about 14 inches in diameter, with sides sloping outwards at an angle of about 30°, is used. The gravel and water are added, reduced to a fine mud and the pan well shaken with a circular and oscillatory motion so as to force the lighter portions out and retain the heavier portions which contain any gold that may be present, water being added from time to time. In some parts a rectangular wooden trough 3 feet by 18 inches, fitted with rockers and termed a " cradle," is used. The gravel is passed through a sieve and falls over an inclined blanket into the cradle, water being added as before. The mud is thrown forward by the motion imparted by a workman, and the metal retained in the bottom. Mercury is sometimes added to amalgamate the gold. The blanket assists in catching any free gold. The "sluice" is used where water is plentiful. It consists of a series of long wooden troughs joined together, having strips of wood fixed on the sides and bottoms in order to retain the gold and other heavy

particles, while the mud is washed forward with a current of water. Mercury is used in the sluice for amalgamating the gold. The amalgam is collected periodically, and after filtration through canvas bags the residue is distilled. In river mining, a portion of the river is dammed and the water diverted, when the gravel in the bed is raised by dredging and then treated by washing in the usual way for the extraction of the gold.

In California and Australia auriferous gravels containing small quantities of gold extend through whole mountain ranges, but they are chiefly concentrated near the "bed rock." Shafts and tunnels are then made so as to arrive at the deposits. In these tunnels sluice boxes are laid 3 to 4 feet wide. The bottoms are composed of thick blocks of wood alternated with stones. In the interstices between these obstructions mercury is placed, sometimes to the amount of 2 tons in a long sluice. All being ready for the removal of the gravel, water is conveyed through iron pipes from a high reservoir to the spot. The end of each pipe is connected with a universal joint, terminating in a nozzle, for the delivery of the water. From these nozzles streams of water are projected against the face of the gravel bank, which is continuously washed away by the force of the water ; the muddy stream thus produced runs through the sluice way, prepared for the purpose, and the obstruction offered to its passage by the projections on the bottom cause the heavier metalliferous portions to be largely retained and the gold to be amalgamated by the mercury. Sluices are often made double, in order that one part may be kept in action while the other is being cleaned out. Sometimes the whole depth of the deposit, down to the bed-rock, is washed away.

The hydraulic elevator is a machine by which a jet of water under high pressure forces water, gravel, and rock up an inclined plane and delivers them at the head of the sluice, which in some cases is 100 feet above the bed rock.

Treatment of Gold Quartz.—This material is very hard and compact, and constitutes the veins of gold ore in which the free gold is present in sharp, angular fragments, as distinguished from the condition of the metal in alluvial or placer deposits. The mode of treatment of gold quartz is somewhat similar to that employed for certain silver ores already described, and consists of first crushing the ore to a very fine state of division in rock breakers, stamps, rolls, etc., and subsequently amalgamating the gold in pans, etc.

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The type of rock breaker generally employed is that of Blake (Fig. 90), in which the ore is broken into pieces about the size of walnuts, and discharged upon a platform immediately in front of the stamp battery.

A Stamp Battery is represented in Fig. 107. It consists of five crushing stamps in one mortar, and in fact acts in the
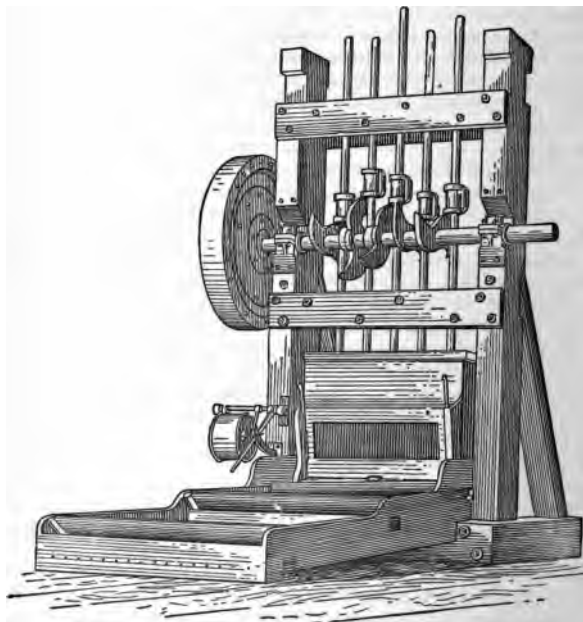
Fig. 107.

same way as an ordinary pestle and mortar. The frame is generally made of timber. The force of the impact of the pestles or stamps is very great, requiring a very solid foundation for the mortar block, which supports the mortar. This is firmly bolted to the block. The battery frame is independent of the mortar block, and, if possible, the bottom timbers are fixed to the solid rock with iron rods. Instead of wood braces, iron rods are frequently used, or a combina-

tion of wood and iron, as they take up less room, and the iron rods are easily tightened (see Fig. 86).

The Mortar is made of a single casting of cast iron about 5 feet long, 4 feet high, and 1 foot wide, weighing from 2 to 3 tons. The bottom has a flange, by which it is bolted to the mortar blocks, and to prevent too great vibration the block contains a layer of blanket or India-rubber between it and the mortar. Fig. 107A represents a mortar employed for wet crushing, having a single discharge. *n* is the feed opening by which the material is conducted into the mortar, *t* is the die which receives the force of the blow ; *d* is the screen which regulates the size of the particles of ore escaping from the mortar. The screens are set in iron frames, which slide in grooves cut in the side of the
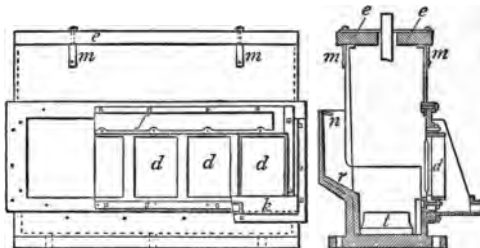
Fig. 107A.

mortar. The screens are made of wire cloth or of sheet iron with holes punched in, varying in diameter from $\frac{1}{24}$ to $\frac{1}{40}$ of an inch, according to the nature of the ore. The mortar is often lined inside with amalgamated copper plates to catch the gold. Sometimes both front and back sides are so lined, and sometimes the screen side only. When the method of dry crushing is adopted, then the mortar is made wider, and has a discharge opening and screen on each side. The width given to a mortar varies with the nature of the ore. Narrow mortars increase the discharge of the pulp from the battery, but if the screens are placed too near the stamps, they are subject to undue wear ; or if the screens are placed too low, they are rapidly destroyed.*

The degree of fineness to which the ore should be crushed depends on its nature and condition. If much pyrites

* See Eissler's *Gold*, p. 30.

rich in gold is present, the crushing must not be too fine. If, however, the gold is present in a very 'fine state of division, the crushing must be fine in order to liberate the gold ; but if the gold is compressed too much by the percussion, it is more difficult to amalgamate.

The drop of the stamps varies from 4 to 18 inches, according to the size. Heavy stamps have the smaller drop and light stamps the longer one, but the drop must be sufficient to produce a good splash, so as to force the ore through the screens. Soft ores and those rich in sulphides should be stamped with a low drop. With a drop of 8 inches about ninety blows per minute are made; and as the height of the drop increases, the number of blows per minute is less. The number of blows generally varies from thirty to one hundred, but it has been proposed to use two cam shafts so as give two hundred blows per minute, and thus increase the yield of crushed ore.

Ore is fed into the mortar by hand, and in some parts by an automatic feeder, which is more uniform. The water required for stamp batteries is allowed to impinge against the stem of the stamp, thus keeping it clean. In front of the mortar is also a water pipe to suppy the necessary water to carry off the pulp down the inclined tables, more water being required here when the crushing is coarse than when it is fine.

Amalgamated Plates.—These plates are made of copper, being $\frac{3}{8}$ inch thick for the mortar and $\frac{1}{8}$ inch thick for the tables outside. These plates require to be of good soft copper. They are first thoroughly cleaned, then coated with mercury until saturated. New plates do not catch the gold well, so that silver amalgam is generally added, and sometimes gold amalgam. The plates of copper are often electroplated before being amalgamated, when they absorb a large amount of mercury, and are very efficacious in catching the gold. In front of the battery are arranged tables to catch the pulp as it issues through the screen. These tables are covered with amalgamated copper plates to catch the gold. They are frequently arranged in a series of steps in order to ensure a more thorough contact of the gold with the amalgamated plates. The largest portion of the gold is deposited on the amalgamated plates inside the mortar, but this depends on the coarseness of grain of the gold, the quantity of mercury added, and on the size and shape of the latter. The inclination of the tables is about $1\frac{1}{2}$ inches per foot.

The material escaping from the amalgamated plates passes to some form of concentrating apparatus, of which one of the best and most widely used is the *Frue Vanner*.

Frue Vanner.—It contains a sloping, endless, india-rubber belt, 4 feet wide, mounted on a frame, and moves up the incline in an opposite direction to the stream of water which flows from the stamps, and carrying with it the suspended gold pyrites. The belt is bounded on the two sides by rubber flanges to prevent the water and ore dropping off. It is subjected to two distinct movements ; a constant direct motion and, at the same time, a lateral rapid side shake. By this means the lighter material is carried forward with the water, and the heavy material travels with the belt in the opposite direction. Fig. 108 shows the main rollers that carry the belt and form the ends of the table, and are of the same diameter. The third roller is shorter than the other two, so that the belt can pass over it without touching the flanges. The belt, in passing below, travels through a tank of water, in which the concentrated ore is deposited. The cranks attached to the crank shaft are $\frac{1}{2}$ inch out of centre, thus giving a lateral throw of 1 inch. Three flat steel springs underneath the frame, and attached to the cranks of the shaft, give a quick lateral motion of one hundred per minute.

Dry Crushing.—Sometimes dry crushing, instead of wet crushing, is resorted to, and then a modification of the apparatus is required. Rolls have been employed in some mills for dry crushing, and it is claimed that several advantages arise from their use. Dry crushing by stamps is one-third more expensive than wet crushing, as the capacity falls off to that extent. The advantage of rolls is in the fewness of the wearing parts and the small cost of repairs as compared with stamps. There is great efficiency in working as there is not the liability to over-crushing, which is the case with a stamp battery. Moreover, the amount of crushing surface in contact with the ore per minute is very large in rolls. The prime cost is also much less. Rolls of special construction have been lately introduced, and doubtless with a certain class of ores there is a great advantage in their use. It is claimed by some workers that the particles of gold are separated from the gangue in a condition better suited for amalgamation than when stamps are used. Rolls are never used for wet crushing.

Formerly various substances were added to a battery to assist amalgamation by their chemical action, but almost the
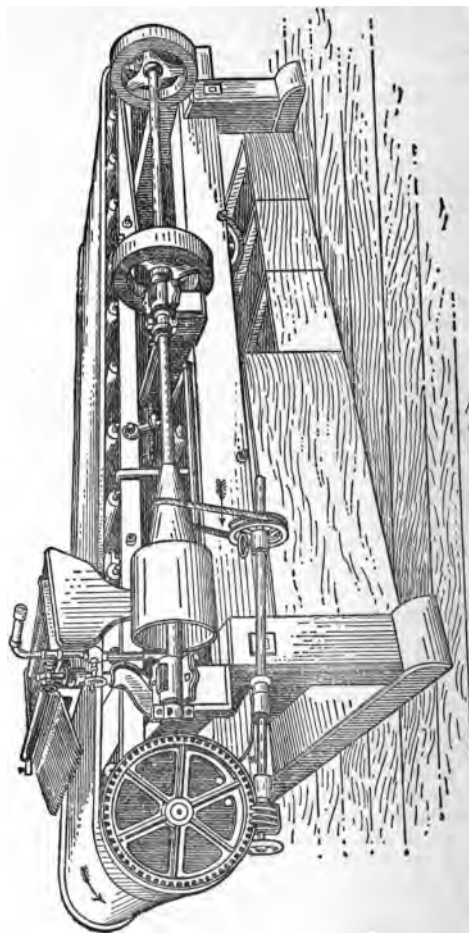
Fig. 108.

only substance employed at the present time is potassium cyanide, which is probably effective in cleaning the plates. The plates may be cleaned from grease, etc., by a weak solution of potassium cyanide. Sodium is used to clean the mercury after retorting, and before using it again in the battery. If base metals are present in the mercury they become rapidly oxidised and cause it to "sicken" and break up into a number of dirty globules, which are not only useless for amalgamation, but are carried away in the tailings and the mercury lost. Mercury is most effective when it contains gold or silver.

Muntz's metal plates are sometimes used for amalgamation in place of copper, but they only take up a small quantity of mercury and require frequent cleaning ; but the cleaning is very easy, and the amalgamated metal plate acts at once in catching gold, without being covered with gold or silver amalgam, which is requisite in the case of copper. Moreover, the mercury on a plate of Muntz's metal is not so easily "sickened" as on copper plates. It probably acts by electrolytic action, the copper and zinc forming a voltaic couple and liberating hydrogen, which reduces the oxides, etc. These plates are cheaper, wear better, and require less attention than copper. They are adapted to ores containing heavy sulphides and arsenides.

Treatment of Concentrates, Battery Sands, Skimmings, etc.—The various concentrates and residues which are obtained after treatment of ores by the preceding operations are submitted to amalgamation in grinding pans, such as the Knox pan (Fig. 87) described in the chapter on silver. The charge of about 300 lbs. is made into a pulp with water and ground for about three hours, when 50 lbs. of mercury are added and the grinding continued for a few hours longer. A little quick-lime assists in the collection of the mercury globules. The pulp is then diluted and discharged into settlers (see Fig. 88).

Retorting.—The separation of the precious and other metals in the amalgam from the mercury is effected by heating in an iron retort. The excess of mercury having been removed by squeezing through wash-leather or canvas bags, the pasty amalgam, rolled into balls, is placed in a pot-shaped, or in a cylindrical retort, which is placed in a furnace and heated. The metal is prevented from sticking to the iron by either placing paper underneath the amalgam or the iron trays may be whitewashed inside. The distilled mercury is condensed in iron cooling tubes, which are surrounded by water.

The amalgam is first heated to the boiling point of mercury, when the temperature is moderated and maintained uniformly for one or two hours, until all the mercury is distilled off. The metal left in the retort is porous and varies in purity from 500 to 950 parts of gold per 1000. The residue being chiefly silver, with some base metals and sulphides. The gold is melted in crucibles with carbonate of soda and borax.

Mr. Rowland Jordon, of London, has introduced an automatic arrangement for the amalgamation of gold ores without the use of fire or water. The ore is first roughly crushed, then passed to a fine crusher in which the ore is subjected to the alternating action of eight flat surfaces of hard iron arranged on two spindles, each revolving with great velocity and in opposite directions. A current of air is drawn in to the chamber by means of vanes on the revolving arms, by which the ore when reduced to powder is carried forward to a settling chamber, and there falls by its own gravity into an apparatus which automatically regulates the feeding of the powder to the amalgamator.

The amalgamator contains a layer of mercury 30 to 50 inches deep, at the bottom of which the powdered ore is delivered, and being lighter than mercury rises to the top. The gold is dissolved by the mercury and the sand carried away by an air current to the waste pit, or, if necessary, to another machine.

Electro Amalgamation.—In the usual method for amalgamating gold ore, in which the crushed mineral is carried over mercury by a stream of water, it sometimes happens that the surface of the mercury becomes coated with oxides, sulphides, or arsenides, which necessitate a strong force of water to remove them, and cause loss of gold. Mercury contaminated in this way is said to be "sick," and requires to be periodically distilled in order to purify it.

Mr. Barker, F.G.S., has introduced a method of preventing this "sickening" of the mercury by connecting the mercury with the negative pole of a battery or dynamo, and the water flowing over it with the positive pole, so that the current flows from the water to the mercury; by this means any oxides, sulphides, etc., are decomposed, and the black scum retreats from the surface of the mercury as if driven by a blast of air.

CHAPTER XVI.

CHLORINATION PROCESS.

PLATTNER, in 1848, introduced the method of treating gold ores with chlorine gas, first for assaying and afterwards for the extraction of gold from its ores and various residues on the large scale. Mr. Deetkin introduced it into California in 1857. It is as follows :

1. The auriferous concentrates are completely oxidised by roasting in a reverberatory furnace.

2. The product is moistened with water and put into a wooden vat, closed with a lid, and capable of holding about 1 ton of material. The inside is made impervious by coating with tar and resin, and the bottom is double, the false one being perforated and covered with gravel and cloth to act as a filter for the gold solution, produced by the action of chlorine gas, which is generated by the action of hydrochloric acid on manganese dioxide and passed upwards through the false bottom.

3. The solution containing gold chloride, which is tapped off from the above vat, is treated with a solution of sulphate of iron, or other suitable re-agent for the precipitation of the gold.

For the proper application of this process the gold must be in the metallic state. If gold quartz containing finely divided gold is employed, it is simply moistened with water and chlorinised without any previous roasting, but if sulphides are present the sulphur must be perfectly roasted so as to convert all base metals into oxides. The chlorine gas employed must be well washed to free it from hydrochloric acid, which otherwise would dissolve oxides and act upon any undecomposed sulphides with the formation of sulphuretted hydrogen, which would precipitate gold as insoluble sulphide from its solution in the vat, while the object of the opera-

tion is to convert the gold into the soluble form. Generally the concentrates containing sulphides from gold mills are treated by the chlorination method, and sometimes certain quartz ores containing free gold. As a general rule it is not advisable to treat gold ores by the above process without submitting them first to concentration, so as to remove as far as possible all worthless material. Besides iron and copper pyrites and arsenical pyrites, the ores often contain galena, blende, or tellurides, etc. By the introduction of the Mears process of using compressed chlorine it has been found possible in many cases even to use the ore direct, after crushing, without concentration. If much silver is present the chlorination is very imperfect unless the metals are in the very finest state of division, as the chloride of silver forms a coating on the particles of gold and protects them from the action of the chlorine. If the gold is in coarse grains it is unfit for the chlorination process, as a very long time would be required for complete conversion into gold chloride. Pan tailings of concentrated sulphides are very suitable for the chlorine process. If the solution contains much lead, it may be precipitated with sulphuric acid and allowed to settle, and the clear liquid run off into another tank before precipitating the gold.

Roasting is performed in various kinds of furnaces, whereby sulphur and arsenic largely escape as oxides, base metals are converted into oxides, and gold remains in the metallic state. If the temperature employed in roasting has not been sufficiently high, some sulphate of iron may remain, and this would subsequently precipitate some of the gold in the chlorination vat. When common salt is added to the charge in roasting, the gold is first converted into chloride, and as the temperature rises this chloride is decomposed by the heat, forming metallic gold.

The ordinary reverberatory furnace was first used for roasting gold ores ; then the double- or triple-bedded reverberatory furnace. The ore is placed on the top bed, to undergo a preliminary drying and heating, while another charge is being finished off on the bottom bed, the waste heat from which is thus utilised. On the middle bed the temperature is intermediate between that of the upper and lower beds. Here the temperature is at a dull red, and the ore loses much of its sulphur, arsenic, etc. ; it is finally raked through the opening on to the lower bed, where the roasting is completed. The bed is made of fire-bricks laid edgewise. There are three or four working doors, which enable the workman

to operate on all portions of the charge. The roof is about
20 inches above the bed. The dimensions vary very con-
siderably in different localities ; some furnaces are 12 feet
square, while some single furnaces are 15 feet wide and 60
feet long. The weight of the charge may be 12 to 18 lbs.
per square foot of floor space, laid 2 to 3 inches deep, the
smaller amount being used when the ore contains much
sulphur. The completion of the roasting may be ascertained
by throwing a little of the ore in water, and inserting a
clean piece of iron. If the iron remains bright, the oxidation
is complete ; but if sulphates remain undecomposed, the iron
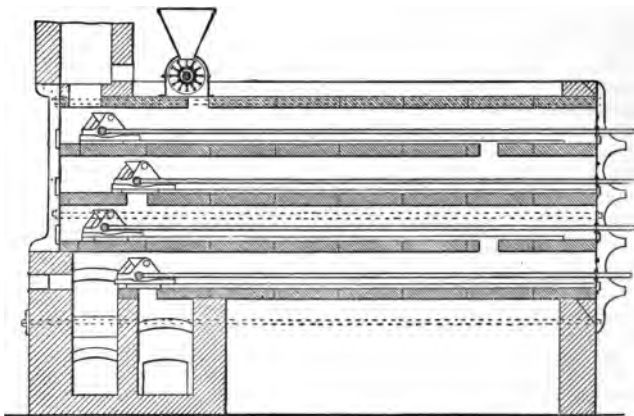
Fig. 109.

is coloured brown. A better plan is to add barium chloride
to the solution, and observe if any barium sulphate is pre-
cipitated, which will indicate the presence of sulphate in the
ore. In the three-floor furnace operating on ores with 20
per cent. sulphur, 8 to 10 hours is required on each floor.

Mechanical furnaces have largely come into use of late
years, of which the Brückner cylinder (Fig. 93) is probably
the most important. The O'Hara, Spence, and White-
Howell furnaces are also extensively used. The Brückner
cylinder is briefly described in the Chapter on Silver, and
the O'Hara and White-Howell are also referred to.

Fig. 109 shows a Spence calciner as improved by Ham-

mond, and is employed in Alaska for roasting gold-bearing
concentrates for treatment by the chlorination process.
About 18 to 20 tons of material per day are treated.   If the
furnace is employed as a pyrites burner for the manufacture
of sulphuric acid, or if the ore contains more than 35 per cent.
of sulphur and it is not injurious to leave 1 or 3 per cent. of
sulphur in the roasted product, then as much as 40 tons may
be roasted per day.   The space required for each furnace
is relatively small, and two men per shift can attend to
six double furnaces.   The area is 34 feet by 18 feet.   One
man keeps the hoppers full, and the other man keeps the
temperature even.   The rakes are actuated by means of a
hydraulic cylinder.   These rakes open the ports for fresh
ore, and discharge the calcined material on to the shelf
below.   With ordinary care the iron rakes will last six
months when salt is used in roasting, and two years when
the ores are roasted alone.*

As already mentioned, common salt is sometimes added to
the charge in roasting certain sulphides.   If the ore contains
lime, talc, or heavy spar for example, it is necessary to use
salt in order to convert these compounds into chlorides, and
save delay and expense in the subsequent chlorination.
Usually about 3 to 4 per cent. of salt is added to the charge
after it is raked on to the lower bed of the triple furnace, or
a few hours before completion in single furnaces.   If silver
as well as gold is present, then a chlorinising roasting is
necessary in order to form silver chloride, since silver is not
attacked by free chlorine at the temperature of the leaching
vat.   The silver chloride is dissolved out by means of a solu-
tion of sodium thiosulphate, or by a saturated solution of
common salt, before extracting the gold.   If much salt has
been used in roasting, it is advisable to well wash the ore with
water to dissolve soluble chlorides before adding the chlorine.
The chemical action of the salt is due to the reaction between
it and the sulphates, thus : $2NaCl + MSO_4 = MCl_2 + Na_2SO_4$.
The sulphur dioxide produced by the roasting also reacts on
the salt in the presence of moisture, with the formation of
hydrochloric acid gas.   These gases act on the ore, forming
chlorides and oxy-chlorides, some of which are volatile and
carry away some silver and gold.   Thus while the formation
of free chlorine is advantageous in chlorinising silver, it
induces its volatilisation.   The best chlorinising effect is
obtained in an oxidising atmosphere ; hence the advantage
of roasting off much of the sulphur previous to the addition

* Peters' *Copper Smelting*, p. 114.

of salt to the charge. When salt has been used, the charge should be allowed to cool slowly in heaps after withdrawal from the furnace. The loss of precious metals by volatilisation increases with an increase in the temperature of the furnace.

Chlorination.—*Vat Process.*—The vat (Fig. 110) is about 7 feet in diameter, made of wooden staves, and 3 to 4 feet high, and capable of holding about 3 tons of roasted ore. The space between the false and real bottoms is about 1 inch deep, and into this space the solution of gold chloride collects, having filtered through the perforated bottom *a.* The false bottom is covered to a depth of $1\frac{1}{2}$ inches with small pieces of quartz, or other hard rock free from lime. On this is placed a series of finer layers of material, the upper one being of sand. The whole thus forms a filter 4 to 5 inches
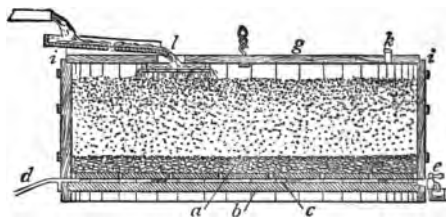
Fig. 110.

thick. The space *c* has two openings, one for the introduction of a lead pipe which conveys the chlorine gas, and at the other side a tap for running off the solution.

The chlorine is generated in an air-tight leaden vessel, and through a hole in the cover passes a vertical leaden rod, terminating in a rake at the end to act as a stirrer. Another opening in the cover contains a lead pipe for conveying away the gas, and through a further opening is inserted a bent tube with a funnel-mouth for pouring in the acid. Water, common salt, and manganese dioxide are first put in, and the cover tightly put in position. Sulphuric acid is then introduced through the funnel, and the contents heated by a small fire underneath. The generator is about 20 inches in diameter and 12 inches deep. The chlorine, before passing to the chlorinising vat, traverses a vessel containing water in order to absorb any hydrochloric acid and other impurities, as far as possible. It is allowed to act on the ore in the vat

for eighteen to twenty-four hours. During the first few hours the lid is left off, and when the smell of chlorine is perceived at the top, the lid is luted on, and the passage of the gas continued for about another twelve hours. The cover is then removed ; if there is a strong smell of chlorine, showing that the ore is well impregnated with the gas, water is added to dissolve the chloride of gold. It is advisable to use only a moderate amount of water, which is added in the form of a spray so that it may slowly percolate through all parts of the contents of the vat.

The action of chlorine on gold is very slow at the ordinary temperature, but as the temperature gradually rises up to 100° C. the rate of combination increases. Rose[*] conducted some experiments at the Royal Mint with chlorine, and also with bromine, to test the rate of dissolution of gold at different temperatures, using the porous gold obtained by parting from silver. The results showed that chlorine and bromine dissolve gold more rapidly at 50° to 60° C. than at the ordinary temperature ; that bromine is much more rapid in its action than chlorine. Deetkin has shown that gold containing base metals is more readily attacked by chlorine than pure gold ; even small quantities of silver increase the solubility of gold, but if much silver is present the gold becomes coated with a film of silver chloride, which checks further action. By the action of chlorine on water, some hydrochloric acid is formed in the vat, and any sulphides are oxidised to sulphate by the liberation of oxygen from the decomposed water, thus :

$$2Cl + H_2O = 2HCl + O$$
$$MS + 4O = MSO_4.$$
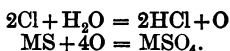
If ferrous sulphate is present through imperfect roasting, the oxygen liberated as above will oxidise it to ferric sulphate. Thus much waste of chlorine occurs by failing to effect perfect oxidation in the furnace, and soluble sulphates, such as those of copper and iron, should be dissolved out by water before submitting the ore to the action of the chlorine. Oxides of base metals are acted upon by chlorine, and still more readily by hydrochloric acid, and it has been found cheaper to dissolve them in dilute sulphuric acid and wash out the sulphates before adding the chlorine gas.

Precipitating Vat.—This is made of the same material as the leaching tubs, and is about the same size. It has no false

bottom, and the sides are sometimes made to incline some-what inwards towards the top, so as to prevent any adherence of gold to the sides. The inside is lined with lead or with a coating of pitch. Some solution of ferrous sulphate is added to the vat ; then the filtered gold solution is added. If the solution requires more sulphate to complete the precipitation, a small portion of it will, on testing, give a brown precipitate, or if the gold is in very small quantity, a dark colouration. When the precipitation is complete, the liquid is allowed to remain at rest for some time for the gold to completely settle.

The Barrel Process.—This was introduced on a practical scale by Dr. Mears in 1877, who accidentally dis-covered that gold ore, when subjected to compressed chlorine, was much more rapidly chlorinised than at ordinary pres-sures. The operation is conducted in revolving iron barrels, lined with lead, instead of in vats. The ore is moistened with water, then charged into the barrel, the air pumped out, and compressed chlorine introduced. The barrel is then kept revolving at a rate of ten revolutions per minute until the gold has been dissolved. An opening in the side serves for charging and discharging the ore. This opening is kept tightly closed during the process. The barrel revolves on a hollow iron axis, and the chlorine is pumped in from a gas holder through a central leaden pipe, and the pressure rises to 50 or 60 lbs. per square inch. By the motion of the barrel every particle is exposed to the action of the chlorine, and as the particles of gold are kept bright by the friction, and any coating of silver chloride is rubbed off, coarser particles can be chlorinised than in the vat process. The objections to Mears' process are : the rapid wear of the vessel ; the diffi-culty of keeping the parts air-tight in consequence of the high pressure ; and·the high cost in repairs.

Adolph Thies, in 1881, greatly simplified the above method by dispensing with the hollow spindle, the pressure pump, and other arrangements for keeping up a very high pressure. He introduced a plain iron barrel lined with lead, with a hole for charging and discharging, and generated the chlorine inside by means of bleaching powder and sulphuric acid. The chlorine is therefore at a very moderate pressure, and although it does not act so rapidly as the externally com-pressed gas, very good results are obtained at a reduced cost compared with the Mears system. The barrel is partially filled with water, then bleaching powder added, then about 1 ton of roasted ore is charged in. To the contents the requisite

amount of sulphuric acid is added, the opening closed, and the barrel rotated as before described. When all the gold is chlorinised, more water is added and the barrel again revolved for some time. The contents are then discharged into filters and well washed to remove all gold chloride, which is precipitated in the usual way by ferrous sulphate.

Newbury-Vautin Process.—This is an attempt to combine the advantages of Mears' and Thies' methods. As pressure increases the solvent power of chlorine on gold, the requisite pressure was proposed to be obtained by the use of compressed air, and the chlorine generated inside the barrel by Thies' method. These experimenters assumed that, as economy is effected by reducing the quantity of chlorine, the compressed air would cause the chlorine to remain in solution and thus act effectively on the gold, which does not appear to be the case. This process has since been much modified, as the original one was not a success.

Swedish, or Munktell Process.—The ore is roasted at a low temperature to convert copper sulphide into sulphate. If silver is present, salt is added to the furnace. The roasted ore is put into vats having false bottoms, the soluble sulphates removed by water and dilute acids, and the copper and silver, if present, precipitated by iron. The residue contains the gold. A mixture of bleaching powder and hydrochloric acid solution is poured on to the mass, and the liberated chlorine attacks the gold, which passes into the solution, from which it is afterwards precipitated by ferrous sulphate.

Electro-chlorination of Gold.—As already mentioned, most metals and many salts deposit gold from its solutions, especially when made alkaline with potassium carbonate, potassic cyanide, etc. The deposition is more perfect when a strong electric current from a battery or dynamo is sent through the liquid.

The Cassel process consists of passing an electric current through a solution of common salt containing gold ore in suspension, by which the salt is decomposed, liberating chlorine ; this dissolves the gold, forming chloride of gold, which is then dissolved by the liquid, and subsequently decomposed, the gold being deposited at the cathode.

The arrangement consists of a vat partly filled with a solution of common salt, and within this a barrel revolves containing the ore. This barrel is perforated with holes and covered with asbestos cloth. The interior of the barrel carries a number of carbon electrodes, connected through the

axis and a rubbing contact with the positive pole of a dynamo machine. The other pole of the dynamo is connected with a large copper plate placed in the outer vat, forming the cathode. By rotation of the barrel, the chlorine separated from the salt comes in contact with every particle of gold and dissolves it. To prevent the precipitation of gold in the barrel by iron salts, lime is added. This method is not a commercial success.

Hauch's Method for Telluride Ores.—This method aims at the production of tellurium as well as of gold and silver, and was introduced for treating certain Hungarian ores which contain about 30 to 40 per cent. quartz ; 10 to 20 per cent. carbonate of lime ; 15 to 20 per cent. carbonate and sulphide of manganese ; 5 to 8 per cent. galena ; 1 to 2½ per cent. copper sulphide ; 5 to 8 per cent. clay ; 1 to 4 per cent. blende, with nickel, antimony, tellurium, gold, and silver. The ore is roasted, during which some of the tellurium is volatilised and condensed in chambers. Part of the gold is reduced to the metallic state, and may be removed by amalgamation. The roasted ore is treated with hydrochloric acid, forming metallic chlorides. The solution is drawn off and sulphuric acid added to precipitate lead and calcium sulphates. These are filtered off and the filtrate treated with ferrous sulphate to precipitate the remaining gold. The solution is again run off into another vat and metallic zinc added, which precipitates the tellurium as a black sponge. This is washed, dried, and melted in a platinum crucible. If the sponge is dissolved in chlorine water and digested for a considerable time with sulphuric acid, pure tellurium is obtained.

Pyritic Smelting.—Hungarian Method.—This consists of fusing auriferous iron pyrites in a blast furnace to obtain an iron regulus in which the gold is dissolved. The richness of this regulus may be increased by fusing it with fresh ores so as to concentrate the precious metal. If the regulus thus formed be roasted, a certain quantity of the sulphur is removed, and on fusing this with fresh ores, the richness may be considerably increased. The regulus may contain 50 ounces of gold to the ton, and is fused with lead or lead compounds, which are reduced, and an alloy of lead and gold is formed, ready for cupellation. This method is but little used.

R

CYANIDE PROCESS.

M'Arthur and Forest patented their cyanide process in 1887, and it is now successfully applied to the extraction of gold from its ore in various parts of the world. That gold is soluble in potassium cyanide is no new discovery, but the practical application of the principle is largely due to the above inventors. It has one great advantage over the chlorine method in not requiring the ores to be previously roasted, while silver is also dissolved. The process comprises : (1) crushing the ore by means of rock breakers and rolls, or in batteries ; (2) leaching the ore in vats, similar to Fig. 110, with a 1 per cent. potassium cyanide solution ; (3) precipitating the gold by means of zinc ; (4) refining and casting the gold into bars. The ore is usually crushed so as to pass through sieves with twenty to thirty meshes to the linear inch. The vats are larger than those used in the chlorination process, and usually hold 10 to 14 tons of ore. In South Africa the capacity is 40 to 50 tons, and in some cases 70 tons. Such vats may be from 16 to 25 feet in diameter, and the very large ones 40 feet in diameter. The false bottom is usually a framework of wood perforated with holes and covered with cocoa-nut matting. The Cassel Company form a false bottom with angle iron, having the angles uppermost and supported on wood blocks. The spaces between the angles are filled with sand, and on this is stretched the canvas. The liquid which collects in the space below the false bottom is run off by an iron pipe, which is closed or opened with a stop-cock. The ore is first well washed to remove soluble sulphates, etc.

The cyanide solution is run on to the top of the ore in sufficient quantity, and allowed to act on it for twelve to twenty-four hours. The action is slow at first, but increases as the operation proceeds, probably from some electrical action between the metals present. The progress of the operation is tested by running off a little of the solution and adding a bit of clean zinc, and if gold is deposited the solution is run off, and pumped back again into the top of the vat or transferred to another vat containing ore, so as to get a good strong solution before depositing the gold. At some works the ore and solution are stirred together by means of an agitator, but the cost through loss of cyanide and the power required may more than exceed the gain through the increase in the yield of gold.

In the case of ore which has been rendered acid by the oxidation of pyrites, caustic soda is added to neutralise it, and the ore washed by running water through it in the vat before adding the cyanide.

The gold is precipitated from the solution by means of zinc shavings, freshly turned in a lathe. These shavings are placed in wooden boxes, 20 feet long, 3 feet wide, and 3 feet high, termed zinc boxes, divided into compartments so as to allow the solution to flow alternately upwards and downwards. The alternate compartments are empty, and the solution is made to flow upwards through the zinc shavings. By this arrangement slimes are prevented from collecting on the upper surface of the zinc and thus impeding the flow. In some cases the zinc shavings are supported on wire-screen trays, so that the gold falls through the screen to the bottom of the box while the zinc remains on the shelf. When sufficient gold has been deposited, the slimes containing the gold are run off through a hole at the bottom of the box, dried in iron pans, and sifted through a fine sieve in order to remove particles of zinc. If the solution contains copper, it is found with the gold.

The precipitate is next melted in plumbago crucibles with sand, carbonate of soda, and borax as fluxes. Zinc is largely volatilised, and the slag consists of silicates of zinc, soda, lead, etc. The bullion thus obtained is sold to gold refiners. The imperfectly fused slag may retain much gold, which is recovered by fusion with lead and cupelling the enriched lead. In some works the slimes are roasted in a muffle furnace to volatilise the zinc before melting in the crucible.

Eissler states that the following conditions affect the cyanide treatment adversely :

1. The action of impurities and base metals in ores prevent the solution of gold, and affect the decomposition of cyanide. This will require a complete study by analysis of the component parts of the ore.

2. It is necessary to examine the condition of gold in residual tailings or concentrates from the cyanide treatment. (a) In this connection it has to be ascertained if a certain percentage of dissolved gold has not been completely washed out ; (b) also, if a certain percentage of gold is still present in coarse particles, capable of being amalgamated ; (c) and the percentage of gold encased in quartz or pyrites to which the solution has not had access ; (d) the occurrence of gold in lumps of slime after treatment by cyanide—the gold is supposed to be precipitated by the action of iron salts, pro-

ducing a ferrous-ferricyanide from auro-potassic cyanide and free cyanide, thus explaining some low extractions from weathered ores and concentrates.

Hannay's Process.—This is a combination of the amalgamation and the cyanide methods. The object is to keep the mercury bright, which is effected by the aid of an electric current. The mercury is placed in a cone-shaped iron pan, which can be rotated by means of a screw propeller at the bottom. On the mercury is poured a solution of potassium cyanide, and on the top of this is placed the crushed ore. The cyanide solution converts the ore into a pulp, and through this an electric current is passed. The mercury forms the negative pole, and a lining, consisting of a mixture of pitch and plumbago, forming a ring round the lower part of the vat, is used as the positive pole. By the motion of the pulp, the free gold is brought in contact with the mercury, and the more refractory particles are dissolved by the cyanide and deposited on the mercury by the action of the electric current. The method has not yet been adopted on the large scale as far as I know.

REFINING AND PARTING OF GOLD.

Impure gold is melted in crucibles, and, if the amount of impurity is small, a little carbonate of soda and nitre will be sufficient to flux it off. If much base metal is present, the gold is partially refined by adding nitre and borax, a little at a time, and skimming off the slag when all action has ceased. This slag is very corrosive, and attacks the crucible, so that a little bone ash is often placed on the top of the metal. The addition of fluxes and the skimming off of the slag is repeated two or three times if necessary. As lead is not easily oxidised by nitre, alternate additions of sal-ammoniac and nitre are made. In the presence of arsenic and antimony, briskly stirring with an iron rod after the addition of a little nitre, will remove them.

Miller's Process.—The method of refining gold by means of chlorine gas was introduced by Mr. F. B. Miller in 1867, and was efficacious in cheaply separating small quantities of silver, which could not be economically removed by the acid process, in Australia and New Zealand. It is very suitable for removing lead, arsenic, antimony, and bismuth, as well as silver, from gold. An ordinary crucible furnace is employed, and the gold is melted in a clay crucible

glazed inside with borax to prevent absorption of silver chloride. The crucible is covered with a well-fitting lid, having a hole in the centre for the admission of a clay pipe, which conveys the chlorine gas to the bottom. The furnace is also covered with a clay tile, also having a hole for the chlorine pipe to pass through. The chlorine generator is placed at the back of the furnace wall in another room, and a lead pipe passes through the wall to convey the chlorine to the furnace. The gold having been melted, the clay pipe, previously made red hot, is pushed below the molten metal and the current of chlorine gas passed into the metal. Dense fumes at once arise, due to the formation of volatile chlorides of the base metals. These fumes are specially dense when lead is present. When the base metals have been chlorinised the fumes cease, and silver is rapidly attacked. As long as any notable quantity of silver is present in the gold, nearly the whole of the chlorine is absorbed. When the operation is nearly over, brownish fumes appear, consisting largely of free chlorine. These are followed by brownish-yellow fumes, and the completion of the purification is indicated by the brownish-yellow stain made on a piece of white tobacco pipe when placed in the fumes. The passage of the gas is then stopped, and the crucible removed from the fire. After the gold has solidified the silver chloride remains liquid, and is poured off into iron moulds, and the solid mass of gold tipped out. A little gold is contained in the silver chloride, partly in shots and partly as chloride. This is removed by melting the silver chloride under a layer of borax and then adding sodium carbonate without stirring. When all action has ceased the temperature is raised; and when the contents are quite liquid, the pot is removed and allowed to cool. The gold is found at the bottom. The silver chloride is poured off, and the gold tipped out as before.

The silver chloride is reduced by means of zinc or by iron. The chloride is cast in slabs and placed in a wooden frame between slabs of zinc, and connected with the zinc by a silver wire. The whole forms a galvanic couple, and, when placed in acidulated water a current of electricity is produced, which dissolves the zinc and reduces the silver chloride to metallic silver. At the Melbourne mint the slabs of silver chloride are placed in flannel bags, and iron plates used instead of zinc. Any copper that is present is reduced with the silver in both cases.

Parting by Sulphuric Acid.—Authorities differ as to the quantity of gold and silver which must be alloyed to-
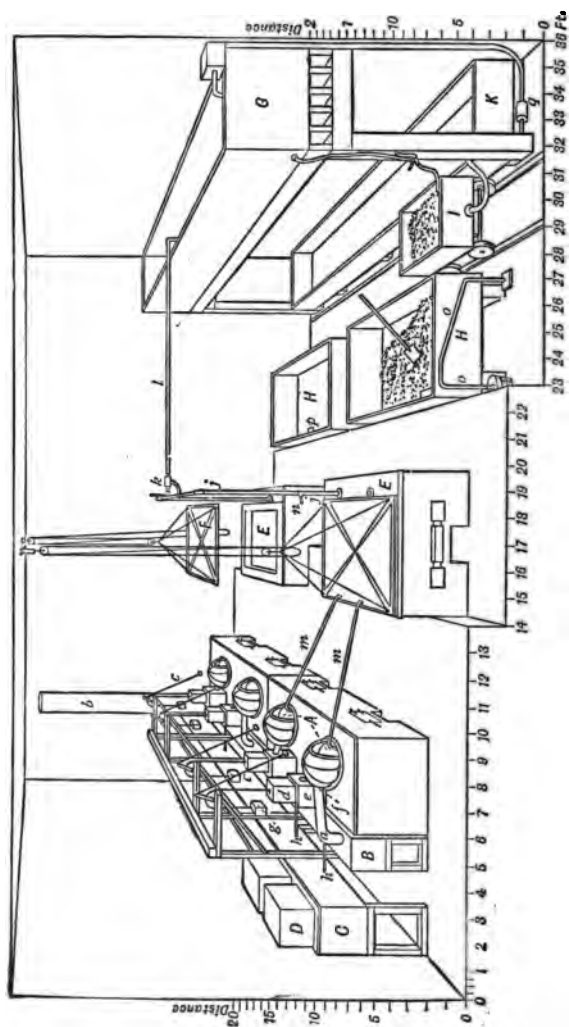
Fig. 111.

gether in order to completely separate silver from gold. Some recommend 1 of gold to 3 of silver, and others 1 of gold to 2½ of silver. The amount of base metals must also be regulated, as certain sulphates are only sparingly soluble in strong sulphuric acid. There should not be more than 10 per cent. of copper and 5 per cent. lead present. ·5 part of gold in 1000 can be profitably parted by this method, while 1 part of gold in 1000 cannot be economically separated by the nitric acid method.

The metals having been alloyed in the proper proportions, the alloy generally is granulated by pouring into water, or it may be cast into bars. The vessels employed for dissolving the soluble metals from the gold are made of fine grained white cast iron, containing 3 to 4 per cent. of phosphorus, which resists the action of the acid sufficiently well when air is excluded. Each pot is covered with an iron lid, capable of being bolted tightly on. Bent lead pipes passing from the lid convey away the fumes of sulphur dioxide, which may be utilised for the manufacture of sulphuric acid. These pots are heated underneath by a separate fire. The charge varies considerably, and may be from 200 lbs. up to 1000 lbs. of alloy. When the silver, copper, etc., are completely dissolved, the retorts are allowed to cool, and this is assisted by adding some cold acid. The solution is then ladled out into lead-lined vats containing hot water, in which the silver is precipitated. The residual gold is again digested with more acid, and finally placed in a filter box and well washed. It is then ready for refining and toughening.

The silver solution on being diluted with water, as mentioned above, throws down crystals of silver sulphate, which are re-dissolved on boiling the solution. The silver is then precipitated by means of copper.

In the *Gutzkow method* of sulphuric acid parting at San Francisco, the bullion treated consists of (1) gold bars containing about 800 or 900 parts gold per 1000, 10 to 20 of base metals, and a little silver; (2) silver bars, termed doré, with 10 to 100 parts gold per 1000; (3) silver bars containing 100 to 800 parts silver per 1000, and the rest copper. The gold bars are alloyed with the necessary silver, granulated and parted. The others are treated in bars. Fig. 111 shows the arrangement of the plant. The boiling kettles are flat-bottomed cast-iron vessels A, each containing 200 lbs. of alloy. The acid comes from the tank c into F by means of the plunger D. At the conclusion the solution is syphoned into E and then into H, where it is cooled to 27° C., and the silver

sulphate crystallised out. The mother liquor is used again in another operation. The crystals of silver sulphate are filtered off into I, and a hot solution of ferrous sulphate run on them from G to dissolve the copper sulphate, and the solution filtered off. After the removal of the copper salt, the silver is reduced by ferrous sulphate or by metallic iron, thus :

$$2FeSO_4 + Ag_2SO_4 = Fe_2O_3 \cdot 3SO_3 + 2Ag.$$
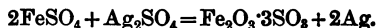
The ferric sulphate which is formed by the above change is boiled with iron in K, and restored to ferrous sulphate.

In 1891 Mr. Gutzkow modified the above method. He uses much more acid than before in proportion to the alloy, and treats 400 lbs. of alloy in each pot. The solution is syphoned off from the parting vessel into a cast-iron pan, cooled by water on the outside, and steam is blown through a lead pipe into the hot liquid to dilute the solution and keep the sulphate from crystallising before the right degree of dilution is attained. Then the steam is shut off, the silver salt allowed to crystallise, and the mother liquor filtered off into a lead-lined box provided with a false bottom and containing precipitated copper. The crystals of sulphate of silver are then removed, dried, and reduced in a crucible by means of carbon.

Parting by Nitric Acid.—In this, as in the former method, it is necessary to have about $2\frac{1}{2}$ parts of silver to 1 part of gold. The metal, having been alloyed in the above proportions, is granulated by pouring into water, and then put into digestors, formerly of glass or earthenware, but afterwards platinum vessels were used. The silver, copper, etc., are dissolved, while the gold is unaltered. The following equations show the changes which occur :

$$8HNO_3 + 6Ag = 6AgNO_3 + N_2O_2 + 4H_2O$$
$$8HNO_3 + 3Cu = 3Cu(NO_3)_2 + N_2O_2 + 4H_2O.$$
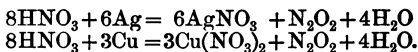
The strength of the acid used is about 1·2 specific gravity, and about 3 lbs. of acid are required for each pound of alloy. About $1\frac{1}{2}$ lbs. and some water are used in the first boiling, which lasts five to six hours, and the solution is then syphoned off. The second addition of acid is much stronger, as the last remnants of alloy have to be dissolved out of the gold. This boiling lasts about two hours. The vessels are provided with hoods, the top of which is provided with a pipe for carrying off the fumes, and recovering any silver that may be carried over with them. The silver solution is

cooled, and treated with common salt, which precipitates the silver as chloride. The silver chloride is reduced by zinc in dilute sulphuric acid and by hydrogen, thus:

$$2AgCl + \quad Zn \quad = ZnCl_2 + 2Ag$$
$$Zn + SO_4H_2 = ZnSO_4 + \quad H_2$$
$$2AgCl + \quad 2H \quad = 2HCl + 2Ag.$$
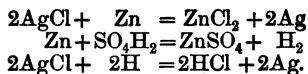
The gold, after parting, is washed to free it from acid and the silver nitrate, after it has been pressed by hydraulic power, is dried, melted, and cast into bars.

Parting by Electrolysis.[*]—A process was patented by Mr. Moebius in 1884, and has been successfully employed in the United States and in Germany. It is suitable for refining copper bullion containing large proportions of silver and gold, together with small quantities of platinum, lead, and other metals, but is chiefly used in parting doré silver. The wooden vats are painted inside with graphite paint, and contain a 1 per cent. solution of nitric acid. The anodes are plates of bullion $\frac{1}{3}$ inch thick and 14 inches square, hung in muslin bags to catch insoluble impurities. The cathodes are plates of silver, the surfaces of which are kept constantly clean by a mechanical arrangement of brushes or scrapers. The loose silver falls on a plate below. Copper is not deposited unless the solution becomes weak in silver and strong in copper. If the copper in the solution becomes large, the silver anodes are replaced by carbon until the silver is deposited, when the carbon cathodes are replaced by copper and a strong current passed to deposit the copper. A current of 1 to 3 volts is used in depositing the silver. It will be seen that, starting with a weak nitric acid solution, silver and copper nitrates are usually formed. The former is decomposed and the latter gradually accumulates, and fresh acid is occasionally added to prevent the copper being deposited. Platinum, gold, and other metals largely remain in the muslin bags.

Certain ancient methods of parting impurities from gold, by heating the gold with certain substances in the form of a powder, and termed the "cement," are now practically obsolete. Some of them are briefly enumerated below.

1. The impure gold was granulated and heated in a clay pot with a mixture of *brick-dust and common salt*. The silver and other metals were converted into chlorides, and dissolved out by salt water.

[*] Gore, *Elec. Separation of Metals*, p. 240.

2. *Sulphur* was used for concentrating auriferous silver so as to form a richer gold alloy.   On fusing such an alloy with sulphur some silver sulphide containing gold was formed. This gold was precipitated from the regulus by fusion with silver, iron, or litharge.

3. *Sulphide of Antimony* was used to purify gold, containing only a little silver.   On melting the gold with sulphide of antimony, an alloy of gold with some reduced antimony was formed, and silver sulphide.   The antimony was afterwards volatilised by a blast of air in a furnace.

CHAPTER XVII.

PLATINUM.

THE great advance made in the metallurgy of platinum in this country, during the present century, is largely due to the work done by the firm of Johnson, Matthey & Co., London.

Platinum is a white metal, with a brilliant lustre ; highly malleable and ductile, as soft as silver, and can readily be welded at a red heat ; it is very tenacious, being only exceeded by iron, copper, and aluminium among the simple metals ; it only melts at the highest temperatures, such as those of the oxy-hydrogen flame and of the electric arc. Violle gives its melting point at 1750° C. It does not oxidise at any temperature, and resists the action of all single acids except boiling pure sulphuric acid, its best solvent being aqua regia. Platinum is dissolved by concentrated solution of potassium cyanide. It is attacked by silica in the presence of carbon. Smoky flames act on it, probably forming a carbide. It is one of the heaviest metals, having a specific gravity of 21·5. Like silver it absorbs oxygen when melted, giving it out again on cooling, causing the mass to "spit." It is capable of absorbing large quantities of hydrogen and other gases when heated, especially the spongy variety termed platinum black ; if this substance is introduced into a mixture of oxygen and hydrogen it causes them to combine with the development of great heat. Two pieces of platinum can be fused together by means of the oxy-hydrogen blowpipe (autogenous soldering). Platinum has a coefficient of expansion about the same as that of glass, hence it can be fused into glass articles. It is a poor conductor of heat and electricity.

Platinum occurs in nature, like gold, in the metallic state, in the form of grains or nuggets, often associated with iron,

copper, gold, silver, and several rare metals, such as rhodium, palladium, etc.

METHODS OF EXTRACTION.

Wet Method.—1. The ore is first washed, and gold and silver separated by amalgamation. 2. The residue is next digested with boiling nitric acid to dissolve out all base metals, such as iron and copper. 3. It is then boiled with aqua regia, forming a solution of platinum chloride. 4. The solution is then evaporated to remove the acid ; re-dissolved in water ; mixed with an equal bulk of alcohol, and a solution of ammonium chloride added, which precipitates the platinum as a double chloride ($2NH_4Cl,PtCl_4$). 5. This chloride is washed, dried, and ignited in a plumbago crucible, when the platinum is left as a black powder. 6. The spongy mass is then welded by heat and pressure into the compact form.

Dry Method.—Deville and Debray introduced the method of extracting platinum by smelting the ore in a reverberatory furnace with galena or litharge, thus forming an alloy of lead and platinum, which is afterwards cupelled. The cupellation cannot be finished in an ordinary furnace in consequence of the high melting point of platinum, so that the refining is completed on the lime hearth of the oxy-hydrogen furnace (Fig. 112). This consists of two hollow blocks of lime placed together and bound with iron.
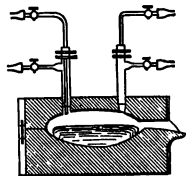
Fig. 112.

The upper block is perforated for the introduction of the blowpipes, one tube of each pair conveying coal gas and the other oxygen. The metal is placed in the cavity of the lower block, and 20 to 30 lbs. may be refined in an hour.

The spongy platinum obtained by the wet method is now melted and refined in this furnace, while, for the purpose of casting platinum into ingots, a crucible of gas coke is used in which the metal is placed ; this is enclosed in a lime crucible, and the whole heated in a lime furnace by means of the oxy-hydrogen blowpipe flame.

To prepare pure platinum from the commercial metal, it is melted with 6 parts of pure lead and the alloy granulated by

pouring into water. It is then digested in dilute nitric acid, 1 to 8 of water, which dissolves copper, iron, palladium, and rhodium, and some lead. The residue may contain platinum, lead, iridium, and other metals. It is digested in weak aqua regia which dissolves the platinum and lead. The solution is evaporated, sulphuric acid added to precipitate the lead, and after filtering, the platinum chloride is diluted, and the double chloride precipitated as in the above wet method by adding ammonium and sodium chloride in excess at 80° C. The solution is allowed to stand several days. The solution is often rose-tinted by the presence of rhodium. The precipitate is fused with potassium and ammonium bisulphates in a platinum vessel, when the small quantity of rhodium present is dissolved out in water, and the platinum is left as a black spongy mass.

Electro-deposition.—There are two names given to the electro-deposition of platinum—platinising and platinating. By the former method is meant its deposition as a dark film, and by the latter its deposition as a white metal. Smee platinised sheets of silver for his battery; and various shades of colour are imparted to different parts of silver goods by painting them with solutions of platinum chloride of different strengths.

A plating solution may be made by dissolving platinum chloride in potassium cyanide. The solution is used warm, with a moderately weak current. The anode does not dissolve, so that the solution must be periodically renewed with fresh platinum salt.

CHAPTER XVIII.

LEAD.

LEAD has been known from remote antiquity, and its use in purifying gold and silver by the process of cupellation is perhaps the oldest metallurgical operation on record. Roberts-Austen says, "Of all chemical phenomena, probably none have contributed more to advance chemistry as a science than those bearing on the relations between oxygen and lead, and the interest attaching to the mutual behaviour of these two elements is so great that the student will do well to consider the influence of this very ancient metallurgical process on the scientific views of the present day." *

Lead has a bluish-grey colour and considerable lustre when freshly cut, but this soon diminishes by superficial oxidation. It is a very soft metal, and can be easily cut into slices (sectile); it therefore readily receives impressions, and leaves a dark-grey mark on paper, and two pieces can be welded by pressure. It is very malleable and also ductile, but the tenacity is so feeble that it can only be made into wire with great care. It emits a dull sound when struck, but it may be made sonorous by casting it in the shape of a mushroom. The presence of certain impurities hardens it and increases its sonorousness, and also its brittleness. It is an easily crystalline metal. If lead is melted and allowed slowly to solidify, the surface and sides become solid first, and if the crust is broken, the remaining liquid portion may be poured off, when the residue will be found crystallised in octahedra. Lead is readily deposited in the form of crystals, from a solution of lead acetate, by means of zinc or electricity. Its specific gravity is 11·35. It begins to fuse at 325° and is completely liquid at 335° C. Its specific heat is ·0314 between 10° and 100° C., and for

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* *Introduc. to Metallurgy*, pp. 2-5.

molten lead ·0402 between 380° and 450° C. It is a poor conductor of heat and electricity. It is without taste, but emits a certain odour when freshly cut. Two pieces of lead may be fused together by a blow-pipe to form a firm joint ; this is termed "autogenous soldering." Commercial lead is frequently almost pure, but sometimes small quantities of silver, copper,.tin, and sulphur are present, and occasionally zinc, arsenic, and iron. All these tend to harden it. Lead exhibits in a remarkable degree the property of flowing when in a viscous state. Lead pipes, rods, etc., are made in machines using hydraulic pressure by what is termed "squirting." A vessel is filled with molten lead and then closed. Through an orifice in this vessel the lead, when just solid, is forced into a steel cylinder, whose bore is the size of the external diameter of the desired rod ; or, if piping is required, a steel mandril of smaller diameter is arranged in the centre of the cylindrical tube, and round this mandril, that is, between it and the interior of the cylinder, the lead is squirted so as to form lead piping. As the piping emerges at the top, it is coiled round a suitable drum. Composition piping, as it is termed, contains tin or antimony, which hardens the lead.

Lead and Oxygen.—Several oxides of lead exist, but only two are of metallurgical importance, viz., litharge PbO, and red lead Pb_3O_4. There are two varieties of the mon-oxide obtained by the oxidation of metallic lead. When the oxide forms below its melting point, it is produced in the form of a brownish-yellow amorphous powder, termed "massicott," but if the temperature is sufficient to melt the oxide thus formed, it assumes the form of a reddish-yellow crystalline mass, termed "litharge." This oxide is produced in large quantities during the process of cupellation, but is then often very impure. The best kind of litharge is manu-factured from the purest commercial lead, which is submitted to cupellation. The first and last portions formed are re-jected, and the remaining portion is collected in iron pots as it is formed, and allowed to cool slowly. When the pots are tilted some of the litharge falls out ; the central portions, which have cooled more slowly, are lighter in colour and scaly in appearance, and sold as flake litharge. The rest remains as a hard mass, and after grinding to powder it is carried by a stream of water into settling tanks. It is then collected, dried in a reverberatory furnace, and sold as levigated litharge. This oxide melts at a red heat to a clear orange-coloured liquid, and if it is in a clay crucible it rapidly

corrodes the crucible. It is a powerful base, and therefore readily unites with silica and other acids. It also dissolves in potash, soda, baryta, or lime water. The ordinary reducing agents, such as carbon, carbonic oxide, hydrogen, cyanogen, etc., readily reduce it to the metallic state. In the case of reduction of oxides of lead by carbon the gas carbon dioxide is formed, because the temperature required to effect the separation of the lead and oxygen is below that at which carbon reduces carbon dioxide to carbonic oxide. Litharge unites with many metallic oxides and forms fusible compounds, but the amount required for this purpose depends on the nature of the oxide to be rendered fusible; thus cuprous oxide requires 1 part of litharge, ferric oxide requires 4 parts, zinc oxide requires 8 parts, and tin oxide requires 12 parts. Litharge acts as an oxidising agent on many metals, such as copper, zinc, iron, etc.

Red Lead (minium), Pb_3O_4.—This oxide is largely manufactured for use as a pigment, for use in flint glass, for a cement in making steam and other joints, for secondary batteries, and in assaying. It may be adulterated with brick-dust or oxide of iron, but they are easily detected by fusing the red lead in a crucible, when it is converted to yellow litharge, but if the above impurities are present they will retain their red colour. The manufacture is conducted in two stages : (1) conversion of lead into massicott, termed "drossing"; and (2) the conversion of the monoxide into the tetroxide, termed "colouring," thus :

$$Pb + O = PbO$$
$$3PbO + O = Pb_3O_4.$$
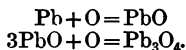
The drossing oven resembles a baker's oven, and is a low arched reverberatory furnace, which is everywhere closed except at the front end, through which the charge is introduced and rabbled during the oxidation. The bed is of cast iron covered with a layer of fire-brick, and made to slope slightly towards a median line and from back to front. On either side is a fire-place with a separate door, divided by a low flue bridge from the bed. The total length is about 11 feet, and the width between the bridges 8 feet. A charge of 25 cwts. of lead is melted, and rabbled for 5 to 6 hours. The oxidation is promoted by adding some slag-lead containing antimony, from time to time, and special alloys of lead and antimony are often used to hasten the process, but the red lead is not so good for making the best flint glass. The charge when oxidised is raked out, allowed to cool, then

ground to a fine powder, and washed with water. A stream of water conveys the powdered oxide into settling vats, and when it has subsided the water is run off and the material is ready for the colouring process.

The massicott is placed n the oven, and quickly dried. It is then spread over the bed in ridges, and carefully heated at a temperature of about 300° C., until the yellow colour has changed to purple, a reaction which is greatly facilitated by careful stirring. When hot the colour is purple, but when the change is complete the mass assumes a bright red colour on cooling. The charge is then withdrawn, re-ground, and sifted, when it is ready for use. It is a granular-crystalline powder.

Lead and Sulphur.—These elements readily unite when heated together, forming lead sulphide PbS, which is a bluish-grey, brittle, and crystalline body, melting at a strong red heat. When roasted in air at a low temperature it is oxidised to sulphate ($PbSO_4$), but at a higher temperature it is converted into oxide (PbO), thus :

$$PbS + 4O = PbSO_4$$
$$PbS + 3O = PbO + SO_2.$$
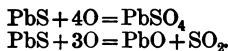
If lumps of lead sulphide about the size of peas be roasted in air, the outer layers will be oxidised, and an inner nucleus of unaltered sulphide will remain. If such a mass be fused, the oxide, sulphate, and sulphide react on each other, liberating metallic lead, thus :

$$PbS + PbSO_4 = 2Pb + 2SO_2$$
$$PbS + 2PbO = 3Pb + SO_2.$$
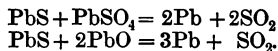
Sulphide and sulphate of lead are most readily reduced by fusing with iron, forming sulphide of iron, which floats as a regulus on the top, and metallic lead, thus :

$$PbS + Fe = FeS + Pb.$$
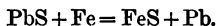
The same effect is produced by oxide of iron and carbon instead of metallic iron. When heated with carbon, or carbonate of soda alone, only a partial reduction of the lead takes place. When lead sulphide is heated with steam it yields sulphuretted hydrogen and lead oxide. The latter then acting on any unaltered sulphide will produce a mixture of lead and lead sulphate.

Lead sulphate is formed as a heavy white precipitate when sulphuric acid or a soluble sulphate is added to a

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soluble lead salt. It occurs as a crystalline ore, termed
"anglesite." It is decomposed when heated with lead sul-
phide, with hydrogen, with iron, and partially by heating
with carbon. Silica decomposes lead sulphate, forming sili-
cate, and metallic lead when heated with it forms lead oxide
and sulphur dioxide.

Phosphorus combines with lead to form phosphides and
phosphoric acid with lead forms phosphates, one of which
occurs in "pyromorphite," an ore of lead.

White lead is a basic carbonate, produced by the action
of oxygen, carbon dioxide, and moisture on metallic lead;
or it is produced by passing carbon dioxide through a weak
solution of lead acetate in which litharge is suspended, or
by passing this gas through a solution of basic lead acetate.
It is frequently contaminated with heavy spar, gypsum, and
zinc oxide.

Lead and Silica.—The oxides of lead and silica readily
combine at a red heat to form a yellow, glassy lead silicate
PbO,SiO_2, but the quantity of base may be varied according
to the relative amounts of lead oxide and silica present.
These silicates become darker in colour as the quantity of
base increases, but the fusibility diminishes with the increase
of silica. Lead silicates are partially reduced by carbon,
and entirely so by iron, or by carbon and oxide of iron. A
mixture of lime and carbon only imperfectly reduce them.
Lead silicate unites with other silicates, with the result of
making otherwise infusible silicates fusible.

Ores of Lead.—The oxides of lead only very sparingly
occur in nature, but the sulphide, carbonate, and phosphate
are very abundant. The chief ore is galena, PbS.

Galena, PbS.—It is frequently found in cubical crystals
and in tabular, reniform or botryoidal masses, also granular,
and sometimes fibrous. It has a grey colour and streak and
metallic lustre, with a specific gravity of about 7·5. It is
sometimes found nearly pure, but more generally it contains
silver, and occasionally gold; sometimes iron, zinc, antimony,
and copper are present as sulphides. Galena melts at a red
heat and easily penetrates clay crucibles. When heated out
of contact with air it volatilises and condenses in crystals.
It is found in Northumberland, Shropshire, Cornwall, North
Wales, and the Isle of Man.

Cerussite, $PbCO_3$, occurs sometimes in transparent, but
usually in white or reddish-white, needle-shaped crystals, also
in other crystalline forms and in stalactitic masses. It gives
a colourless streak and has a specific gravity of about 6·5.

It sometimes contains silver. It occurs in Derbyshire, Cornwall, Spain, the United States, and Australia.

Anglesite, PbSO₄, occurs as a white, grey, or greenish mineral. It is found in crystals and massive, generally associated with galena. It is very brittle and has a specific gravity of 6·2. It has a vitreous lustre.

Pyromorphite, 3Pb₃P₂O₈ + PbCl₂.—It is known as green linnet, brown lead ore, etc. It is white, green, brown, or yellow, according to the purity, and sometimes colourless and transparent. It often occurs in crystals of the hexagonal system, sometimes granular and sometimes massive. It has a specific gravity of 5·5 to 7, and generally a resinous lustre. It occurs in most of the British lead districts, in Germany, France, and the United States.
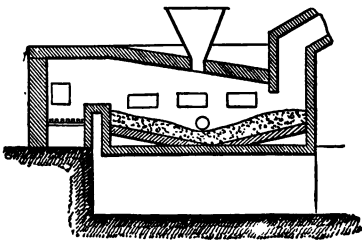
Fig. 113.

Mimetesite, 3Pb₃As₂O₈ + PbCl₂, has somewhat similar appearance and properties to pyromorphite, but is seldom green in colour, being generally grey or brown. Its specific gravity is rather less than that of the phosphate. Many other compounds of lead occur in nature, but the above are the chief sources of the metal.

METHODS OF LEAD SMELTING.

The processes employed for the extraction of lead may be summarised thus :

    I. *Roasting and reaction, or air reduction.*
    II. *Roasting and reduction by carbon.*
    III. *Iron reduction, or precipitation method.*
    IV. *Reduction of oxidised ores and products by carbon.*

Method by Roasting and Reaction.—This is carried out in reverberatory furnaces, of which the Flintshire furnace may be taken as a type (Fig. 113). The length of the hearth is 11 feet and the width 9 feet, and the base is made of slag, moulded to the proper form when in the plastic

condition. The roof is low and inclines from fireplace to flue, and contains in the middle a hopper for charging. Three working doors are arranged on each side, the front being used for rabbling the charge and the back for tapping the slag. The fire-bridge is hollow, about 2 feet wide, and the top is 12 inches below the arch. The bed is made to slope from all parts towards a depression called the well, in front of tap hole, which is placed under the middle door on the front side ; in this well the metal collects before tapping.

The process is conducted in four stages : (1) roasting ; (2) reduction ; (3) stiffening with lime ; (4) tapping the lead and removing the grey slag.

About 1 ton of galena is charged through the hopper and roasted for two hours on the raised part of the bed at a temperature below its melting point, with constant stirring to prevent clotting, when sulphur dioxide is liberated, and a mixture of sulphide, oxide, and sulphate of lead remains. Then the fire is made up and the temperature raised until the charge melts; the reaction between the sulphide and oxides now takes place with the separation of metallic lead, which collects in the well. The mixture of slag and undecomposed ore is then stiffened by mixing with lime (called " setting-up "), roasted again for an hour, and then melted, by which a further separation of lead is effected. The charge is now tapped into a pot outside, heated by a separate fire, the lead being covered with fine coal. It is then well stirred, skimmed, and the metal cast into moulds. The slag, termed " grey slag " is withdrawn in pasty lumps, and the surface of the metal in the tapping pot is covered with slag and regulus. These contain lead, which is separated by stirring with a pole and by throwing on the molten mass coal slack, which is well agitated with the lead. The whole operation of working off a charge lasts about five or six hours.

In some Flintshire works the ore is calcined in a separate furnace, then put into another furnace for reduction by reaction and partly by the addition of iron and carbon as in the old Cornish method.

In Brittany the furnace used for lead smelting is smaller than that of Flintshire, having three doors along one side only. The ore is galena, with 12 to 18 per cent. of iron pyrites, but the method pursued is similar to that in North Wales. The lead obtained is purified by stirring with a pole of green wood as in copper refining.

French Method. —This is a modification of the Flintshire process, used at Couëron. The furnace (**Fig. 114**)

has a hearth or laboratory supported on iron bars, on which are placed firebricks, set on edge, and further differs from the Flintshire furnace in having the lead pot near the flue end. This gives more space for roasting, and the lead collects in the coolest part of the bed. A is the fireplace and C the well for the lead and the tap hole, *a, a,* are the working doors. The principle of the process consists of partial oxidation, followed by reduction at a higher temperature. The ore is charged through the hopper and spread evenly over the higher parts of the hot bed. The fire is now regulated by the damper so as to keep the charge from fusing or clotting. The mass is occasionally turned over by the workmen, and at the end of about an hour the doors are
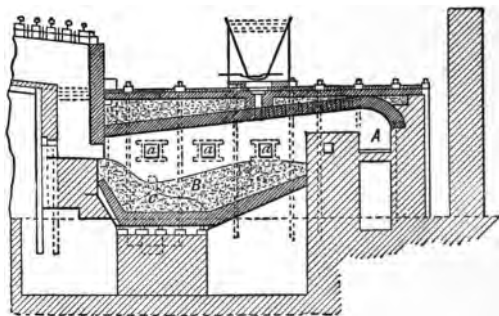
Fig. 114.

opened to admit air for free oxidation, and the mass is then frequently raked and stirred so as to expose all portions equally to the air. When sufficient of the ore has been oxidised the fire is made up and the dampers opened, the doors being now closed. The sulphide and oxides in the roasted mass soon begin to react on each other, but if the temperature is allowed to get too high undue loss of lead occurs by volatilisation. The mass is not allowed to liquefy as in the Flintshire method, and this is prevented by the addition of lime ; the lead, therefore, is reduced, and flows away from the ore without the remaining mass becoming liquid. The first tapping is made in about three hours after the commencement of the reduction stage. A thick dross rises to the surface of the lead and is skimmed off. Coal is then thrown in and the metal well agitated with a paddle.

It is then skimmed and ladled into moulds. The skimmings are now added to the furnace charge, and the reaction continuing, a further quantity of lead is reduced. The grey slag is raked off when reduction is complete, and the metal tapped as before. This process is characterised by a long preliminary calcination, and a reduction of lead without melting of the ore.*

In Spain a reverberatory furnace is employed for smelting rich galena by the method of roasting and reaction, but a kind of blank furnace is placed between the reduction chamber and the stack for the better control of the draught. Also the thickening is made with charcoal instead of lime. In other respects it resembles the Flintshire method. The furnace is termed a "Boliche." It contains two arched chambers separated by a wall, in which are two flues communicating with both chambers. The first is the reduction chamber. The fuel used is wood. The bed slopes from back to front, where it forms a well for the reduced lead to collect. The reduction chamber is lined with fire-brick, and has only one door.

Bleiberg or Carinthian Method.—The furnaces employed are built side by side. The laboratory is 10 feet long and 4½ feet wide at the end near the fire-place, which is a long narrow chamber along one side of the furnace, but only the back part receives the fuel. The bed slopes from the back and from the two longer sides towards a depression in the front end of the bed, and from thence it inclines towards the lead pot in front of the working door. The fuel employed is wood or brown coal. The galena is associated with cerussite, anglesite, and molybdate of lead. The charge is about 4 cwts., and is first calcined, as usual, for three hours, and the temperature is subsequently raised to bring about the reaction between sulphide and oxides. When the lead ceases to flow from the ore, the residue is thickened by ashes and charcoal, and then raked out. The mixture of slag and charcoal, when sufficient has been produced, is strongly heated in the furnace with frequent rabbling, whereby the oxidised compounds of lead are reduced by the carbonaceous materials.

Cornish Process.—This method, which was carried out in Cornwall and some Continental works, was employed for the treatment of impure galenas containing blende, iron ore, fahlerz, quartz, fluor-spar, etc. The reduction was effected partly on the principle of reaction and partly by iron and carbon, so that three products were obtained—lead, regulus,

* Thorpe's *Dictionary of Applied Chemistry.* Article "Lead."

which is again treated for lead, and slag. The ore from
1½ to 3 tons was calcined in a separate furnace, then intro-
duced into a furnace similar to the Flintshire furnace for
reduction, and called the "flowing" furnace. A considerable
quantity of lead was separated by the reaction of the sul-
phide and oxides, and was tapped out. The residue was then
mixed with anthracite and iron, and the temperature raised,
when a further reduction took place, yielding lead, regulus,
and slag. One operation in the flowing furnace took seven
to eight hours.

In the north of England a small blast furnace has been
much employed for lead smelt-
ing, called the "ore hearth" or
Scotch furnace (Fig. 115). It
consists of a small rectangular
chamber, 2 feet × 1 foot × 2
feet deep, lined with cast-iron
plates and closed by an
arched hood for taking away
the fumes ; in the back wall
is fixed a twyer for intro-
ducing a blast of air. In
front is an inclined work
stone b with gutters for the

Fig. 115.

lead to flow into the pot a placed in front of the work stone.
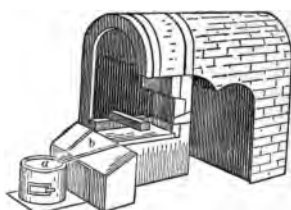
Peat, which is used as the fuel, is first charged into the hot
hearth, and the blast turned on, then a little coal is added,
and then the ore, which was formerly added in the raw state,
but is now first roasted in a reverberatory furnace. In half
an hour the lead begins to separate, when the contents are
well stirred, and a portion thrown on to the work stone b ;
the lead runs into the pot, the grey slag is separated, and
the residue returned to the hearth, and mixed with lime ;
this is repeated at intervals, fresh fuel and ore being added
as required. After some time the cavity of the hearth
becomes full of lead, which flows along the gutters in the
work stone into the lead pot. Two or three tons of lead are
thus produced in about twelve or fourteen hours. This
furnace is employed for poor ores where coal is scarce and
peat plentiful. This process depends partly on the principle
of roasting and reaction, and partly on the reduction by
carbonaceous matter.

The American ore hearth is similar in construction and in
the principle of its action to the Scotch hearth, and so con-
structed as to employ hot blast, produced by causing the air

to travel through the space between the double iron walls of
the hearth, thus helping to keep down the temperature
of the sides while it contributes to the heat in the furnace.
The bottom is also made of iron, 24 inches square and 12
inches deep.   In front is a sloping work stone with a channel
along which the lead flows into the pot in front.   The fuel is
wood or charcoal, and the reduction is effected partly by
roasting and reaction, and partly by carbon.

Iron Reduction Process in Cupolas.—This method
is adopted for the reduction of refractory ores, slags, and
various products obtained in lead refining.   The substance
is either smelted direct, or it is submitted to a preliminary
roasting.   The reducing agent is chiefly iron, assisted by the
carbonaceous materials used as fuel.   Iron is not much used
in the metallic state, as iron ores, hammer scales, refinery
slags, etc., being easily reduced by carbon, the liberated iron
reduces the lead compounds.   In the case of sulphides iron
combines with the sulphur, forming ferrous sulphide, and
liberates the metal.   Iron also decomposes lead silicate with
the production of metallic lead and silicate of iron.   These
reactions, however, are seldom complete, especially as the ores
treated are often very complex, containing copper, iron, zinc,
etc., so that the following products are generally obtained
as the result of smelting in blast furnaces : (1) impure lead,
which often contains the precious metals ; (2) regulus, or
matte as it is also termed, consisting of sulphide of iron with
sulphides of copper and other metals : this floats on the
top of the lead when the metal is tapped, and being brittle
when cold, can be readily separated ; (3) slag, chiefly a
silicate of iron, but in the first or raw smelting the slag
very often contains sufficient lead and other metals to pay
for its re-treatment for their recovery.   Sometimes a fourth
product is obtained when arsenic and nickel are present, as
these metals unite to form nickel speise.

The regulus is usually roasted and smelted in a cupola
with the production of lead, regulus, and slag, as in the first
case, but the lead is more impure, and the regulus often
rich in copper.   The slags are smelted in a small blast
furnace, termed the slag hearth.   In the case of ores which
have undergone a preliminary roasting, where the sulphides
have been largely converted into oxides and sulphates, the
product is smelted with fluxes and reagents, of which iron is
an essential constituent.   The oxidised compounds are partly
reduced by carbon and carbonic oxide duri   ⬛   e melting-
down stage, and partly by iron, which, in ⬛   ⬛ resence of

carbon, easily decomposes lead silicate. In the absence of sulphur, the products are lead and slag.

The older furnaces employed for smelting lead ores, such as the Castilian furnace (Fig. 117), have largely given place to furnaces of the Rachette type (Fig. 46), which enables the blast to penetrate to every particle of material in the hearth, and also causes the ascending gases to travel up the centre rather than up the sides of the furnace, which they are prone to do in cylindrical furnaces. The Rachette furnace is used in the Harz and other parts of Germany. The furnace is oblong and rectangular in shape, being about 3 feet at the twyers, 5 or 6 feet at the throat. The blast is introduced through six or eight twyers, three or four being placed on either side of the hearth, thus causing a better distribution of the air. The Pilz furnace (Fig. 98) is a lead furnace with a greater diameter at the top than at the bottom, but the section is round or octagonal. These modern blast furnaces are now often built with a double iron casing round the hearth or hottest part, and arranged for a current of water to constantly flow through the hollow part. This is termed a " water-jacket."

Silesian Process.—This old method of lead smelting, as carried on in Upper Silesia, was conducted in a low rectangular blast furnace, communicating at the top by means of a circular flue with condensing chambers for lead fume. The blast was supplied by a single twyer fixed in the back wall. The hearth was lined with a brasque of clay and coke dust, and communicated with a fore hearth, through which the slags were drawn off. The charge consisted of 100 lbs. ore, 12 lbs. iron slags, and 30 lbs. lead slags, requiring 1 ton of coal per ton of ore. The products were a rich argentiferous lead, a regulus which was roasted and re-smelted, and a clean or unclean slag according to the content of lead. This method is now abandoned.

Lead Smelting in the Harz.—This is a method of iron reduction, or of roasting and subsequent reduction, in the Rachette type of furnace. Lead ore and lead regulus are roasted in heaps or in reverberatory furnaces. The roasting in heaps takes much longer, but immense quantities can be operated upon at a time. The ground requires to be thoroughly dry, and the ore so placed ⁱt   m   ɪe can be absorbed from the grou   ed and covered with broken ·   ⁱ foundation about 2 or ⸱ a clayey loam or g

and well rolled, so as to form a hard and compact bed. A layer of wood is then placed on this bed, and on this lumps of ore about the size of a man's fist, and on the top of this the main mass of ore or regulus, broken into lumps about the size of walnuts, is placed. The heap is then covered with a layer of finely divided ore to prevent too rapid combustion. It is very important to have the whole space well drained, and to carry off any water the ground is sometimes made to slope towards one side. The pile may contain 100 to 200 tons of material, and measure 30 feet in length, 20 feet in width, and 5 feet in height. The wood is lighted and the current directed to any particular portion by opening vents in different parts of the heap. The temperature is soon sufficient to burn some of the sulphur, and the heat is maintained in this manner. The complete covering with fine ore is often completed after the fire is well ignited, and the bottom portion is kept well open for admission of air. With some ores, and with a sluggish draught, the sulphur condenses in a thin layer, and, upon melting, cakes the finer portions of ore together and prevents its oxidation. The first firing lasts three to four weeks, when the heap is broken up and the well roasted ore is separated from the imperfectly roasted portions, which are submitted to another operation. Imperfect roasting is detected by the presence of more or less fused materials at different parts of the pile, while the more perfectly roasted portions will present a brownish-grey, earthy appearance. By the above roasting process the sulphide of lead is converted into a mixture of oxide and sulphate. Sulphide of iron is changed to sulphate, and lastly into oxide, if the temperature is sufficiently high. Sulphide of copper is changed partly into oxide and partly into sulphate. Plattner states that lead sulphide, after the first firing, contains a white powdery lead sulphate in the interstices, and in places where the temperature has been high crystals of lead sulphate are often found. He supposes that lead sulphide is first sublimed and afterwards oxidised while in the state of vapour either by air or by sulphur trioxide. The outer part of a thoroughly roasted piece of ore is richer in lead on the outer portion than in the interior. Such a piece, if it contains silver, will contain the least silver in the central portion. With regard to heap roasting, Plattner says, " The heap should not be too low, or too flat, as it is desirable that the vapours should be condensed in the upper part ; on the other hand, if it be too high, the circulation of air will be too active."

The ore is smelted in a Rachette type of furnace with basic iron silicate, which is the slag obtained in iron refining. The reactions have already been explained, and the following equations will show the action of the silicate :

$$2FeO,SiO_2 + PbS = PbO + FeO,SiO_2 + FeS$$
$$PbO + C = Pb + CO.$$
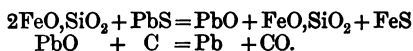
The products are : (1) argentiferous lead, which frequently contains gold ; (2) regulus, chiefly of lead and copper ; (3) slag, consisting of silicates of iron, aluminium, lead and copper oxides. The treatment of these products has been referred to in a previous process, and need not be repeated here.

Swedish Method.—The ore is chiefly argentiferous galena, and was formerly smelted in two operations, known as " raw " smelting and " lead " smelting, in furnaces similar to Figs. 124 and 125. In the former, poor ores and various residues are smelted with iron pyrites, quartz, and lead slag in a blast furnace using charcoal fuel, and producing an argentiferous regulus and a clean slag.

In the lead smelting, rich ores and products, together with the roasted regulus from the raw smelting, some slag, and a little roasted iron pyrites are treated, producing three products : (1) argentiferous lead ; (2) sulphide of iron ; (3) slag, which is chiefly a silicate of iron and lime. The reduction of the galena is effected by iron reduced from the roasted pyrites by means of carbon ; the sulphur of the galena unites with the iron, and some of the iron being oxidised, is, together with the lime, fluxed by the quartz. The following equations will explain some of the chemical changes :

$$Fe_2O_3 + 3C = 3CO + 2Fe \ ;$$
$$Fe + PbS = FeS + Pb \ ;$$
$$FeO + CaO + SiO_2 = FeO,CaO,SiO_2.$$
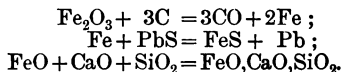
At Clausthal the ores are argentiferous galenas associated with copper pyrites, fahlore, blende, spathic iron ore and pyrites, and a gangue of quartz, calc spar, heavy spar, clay-slate, etc. The lead varies from 50 to 73 per cent., and the silver from ·185 to ·555 per cent. The ore is smelted with basic iron silicate in the blast furnace represented in Fig. 116, which is of the Rachette type. The furnace gradually widens from the twyers to the mouth, and is fitted at the top with a charging cylinder, in the centre of which is a pipe for carrying off the waste gases. The height of the furnace is 25 feet, the diameter at the twyers 3 feet, and at the top

5 feet. The bottom is lined with a mixture of clay and coal dust, resting on a slab of sandstone. There are four twyers arranged round the hearth, and fed from a blast main 5 feet in diameter. The materials to be smelted consist of ore, lime, roasted regulus, and rich slags. The charge, consisting of ore and flux, is put into the furnace in alternate layers, with coke as fuel; and the products, as is usual in iron reduction methods, are lead, regulus, and slag. The following is an example of a charge for the above furnace:
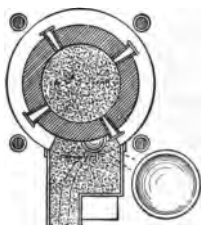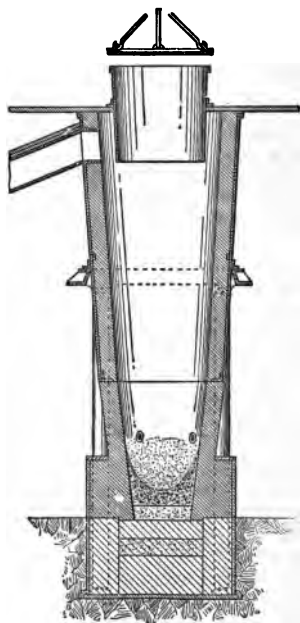
Ore,	.	.	.	100 cwts.
Lead fume,	.	.	1	,,
Lead skimmings,	.	2	,,
Roasted regulus,	.	48	,,
Copper slags,	.	60	,,
Lead slags,	.	58	,,
Regulus slags,	.	42	,,
			311	,,

The argentiferous lead is de-silverised by the Parkes' process. The regulus is roasted in heaps, as previously described, and then smelted. The slags consist of silicates of iron, alumina, lime, and small quantities of zinc, copper, manganese, and magnesium oxides.

At Pontgibaud a highly siliceous galena, rich in silver, is smelted. The ore is first calcined in a reverberatory furnace, 40 feet long × 15 feet wide, having six doors on each side. The ore is charged through a hopper at the flue end, and gradually

Fig. 116.

raked forward as the roasting proceeds. The front part of the bed near the fire bridge is 6 inches lower than the other part ; here the heat is sufficient to melt the charge, which is tapped at intervals of six hours. The roasting converts the galena into oxide and sulphate, and in the final melting a silicate of lead is also formed, which was formerly smelted in the Castilian blast furnace, shown in Fig. 117.

Fig. 117.

The furnace was constructed of blocks of lava bound with iron. It was about 12 feet high × 3 feet wide, supported on iron pillars. The hearth contained three twyers.

The roasted and fused mass was mixed with 10 per cent. scrap iron, 16 per cent. limestone, and 3 per cent. fluor-spar, together with some slags from a previous charge, and various residues. The products were impure argentiferous lead, 7 to 10 per cent. of regulus, and a silicate slag. The reduction may be represented by the equation :

$$2PbO,SiO_2 + Fe_2 = 2FeO,SiO_2 + Pb_2.$$
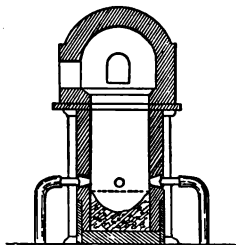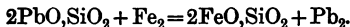
Freiberg Method.—The system adopted at Freiberg differs from the methods already described, in roasting the ores as completely as possible before reduction in the blast furnace, but as the roasted ore still retains 5 per cent. of sulphur, and pyritic ores are added to the furnace charge, the products of the smelting are lead, regulus, and slag, as in other iron reducing processes. The ores treated are of a very mixed nature, comprising lead ores, copper ores, arsenical ores, zinc ores, pyritic ores, and silver ores, besides various residues from the different operations (see Fig. 97).

For the purposes of roasting, the ores are divided into two classes : (1) those containing 20 per cent. of sulphur and under 25 per cent. of lead are submitted to a preliminary roasting in a Gerstenhöfer kiln ; (2) other ores which are roasted in a long bedded reverberatory furnace, together with the partially roasted ores of the first class. The reverberatory furnace will roast 180 cwts. per day. The charge may be mixed in the following proportions—2500 parts roasted ore, 3000 parts raw ore, and 800 parts of residues. In this furnace the ores are introduced at the flue end and gradually pushed forward, as the roasting proceeds, towards

the fire end, so that it travels over areas of gradually
increasing temperature until it reaches the hottest part,
where a partial fusion takes place, and silicates are formed
by the union of silica with metallic oxides.   The charge for
the final roasting consists of 60 per cent. raw ore and 40
per cent. roasted ore.   This finally roasted ore, to give the
best results, should contain not more than 25 per cent. lead,
not more than 10 per cent. of zinc, which thickens the slag,
and about 20 per cent. of silica.   Both the kiln and the
reverberatory roasters are in connection with a sulphuric
acid chamber for utilising the sulphur dioxide.   The roasted
ore is smelted in the Pilz blast furnace (Fig. 98), which is
described in the Chapter on Silver.   The lead obtained con-
tains many impurities, such as tin, antimony, arsenic, copper,
iron, bismuth, and sometimes nickel and cobalt. The regulus
also contains about 20 per cent. of lead.   The slags are
mixtures of three equivalents of monosilicate and one equi-
valent of bisilicate, and when they contain not more than $1\frac{1}{2}$
per cent. of lead and ·002 per cent. of silver they are thrown
away.   The slags from ore smelting usually contain 4 to 5
per cent. of lead and ·01 to ·02 per cent. of silver, and are
smelted in a blast furnace with other products, when lead
regulus and slag are produced.   This slag is generally
sufficiently poor to be thrown away, or is used for building
purposes.   The regulus is rich in copper and lead, and
treated as the regulus from No. 1.   The lead in this case
is very impure, and is submitted to the process of liquation.*

In Colorado lead ores are smelted in furnaces similar to
the Pilz furnace with water jackets, and provided with
what is termed a syphon-tap.   This is an inclined channel
passing into the bottom of the furnace and through which
the lead rises into a basin placed outside the furnace to
receive it.   The ores are "sand carbonates" ($PbCO_3 + PbCl_2$)
and "hard carbonates" (silicious material containing
$PbCO_3 + PbCl_2$, and hydrated oxides of iron and manganese).
Argentiferous galena is also sometimes present. The ores
are smelted with coke, using limestone and oxide of iron as
fluxes.

Lead Fume.—The gases and vapours arising from lead
smelting furnaces contain considerable quantities of lead,
which are recovered by condensing the fume in suitable flues
or condensers.   The most common method is to construct
slightly inclined brick flues, which wind about in a serpentine
manner, generally up the sides of a hill, the whole course

* See *Introduction to Metallurgy*, Roberts-Austen.

extending in some cases for several miles before the vapours escape into the atmosphere; doors are fixed at intervals for purposes of cleaning them out.

Another class of condenser consists of a divided chamber, containing water at the bottom, through which the vapours are drawn several times by means of a pump or other exhauster. Fig. 118 shows Stagg's arrangement.

In Stokoe's arrangement the gases are drawn off by means of a fan and then forced through a condenser, which consists of two chambers placed side by side and divided into compartments by partitions which alternately reach to the top and dip below the water at the bottom of the chamber. Each chamber is divided horizontally by two floors made of open joists and covered with faggots to form filtering beds. A spray of water falls on them from a cistern at the top. The gases meet, in their passage, a fine spray of water, and are
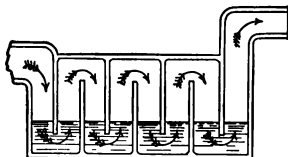
Fig. 118.

compelled to pass through several filtering beds. When the water reaches a certain height, it is run into tanks for the suspended matter to settle out.

The application of electricity to the condensation of fume has been tried and patented by Walker. The flues are partly lined with spikes, and well insulated netting studded with spikes is hung in the middle of the flue. These nets are kept alternately positive and negative. These conductors are connected with an electrical machine, and the fume is stated to be condensed by the continual brush discharge from the conductors. The great difficulty is in keeping the conductors insulated.

Lead fume consists of lead sulphide, oxide, carbonate, and sulphate, and sometimes silver, together with carbonaceous matter, lime, alumina, oxide of iron, silica, etc.

This condensed fume is treated with slags and other products in the slag hearth or furnace, which is generally a small cupola blast furnace, producing an impure lead known as "slag lead." The reduction of the lead compounds and

the scorification of the impurities is effected by means of coal
or coke and iron slags. The lead obtained is hard from the
presence of sulphur, antimony, copper, iron, etc., and re-
quires to be purified, which is effected in a reverberatory,
known as the "lead softening," furnace.

ANALYSES OF LEAD FUMES FROM VARIOUS SOURCES.

Lead oxide, . . .	46·54	10·20	62·26	—
Lead sulphate, . . .	4·87	65·60	1·05	39·00
Lead carbonate, . .	—	—	—	35·80
Lead sulphide, . . .	—	1·40	—	4·50
Iron oxide and alumina, .	4·16	3·40	3·00	—
Zinc oxide, . . .	1·60	13·80	1·60	5·00
Lime, ...	6·07	—	3·77	—
Sulphur trioxide, . .	26·51	—	25·78	—
Insoluble residue, . .	10·12	5·60	1·97	13·20
Arsenic oxide, . . .	—	—	—	2·50

Reduction of Oxides.—Oxidised ores of lead, litharge
from cupellation, pot skimmings, etc., are reduced in this
country in a reverberatory furnace, the bed of which is made
to slope from the fire-bridge to near the flue, where an iron
gutter conveys the reduced lead from the furnace to a pot
outside. The bed is first covered with small coal, which is
coked by the heat, and on this the ore and fluxes, usually
lead slags, are charged. Sometimes oxide of iron is added,
and in the case of heavy spar being present, fluor spar is also
introduced as a flux. The charge is spread over the bed, the
doors closed, and the temperature gradually raised. The
mass is stirred from time to time. The reduction soon
begins by the action of carbonic oxide, formed by the oxida-
tion of the coke, on the oxide of lead. The molten lead
trickles through the porous mass, runs towards the iron
gutter, and thence into the lead pot.

The residues, slags, refractory ores, etc., are generally
reduced in a small blast furnace with coke, yielding very
impure lead and a poor slag, which is of no further use.
The old English slag hearth is a small rectangular furnace,
2½ feet from back to front and 2 feet from side to side, while
from the hearth to the charging hole is about 4 feet. The
top is covered with an arch. The bottom of the shaft has a
slanting iron plate which inclines towards an opening,
through which the reduced lead flows into an iron trough in
front. In front of the lead tank is another tank to receive

the molten slag. In working, the iron bed plate is covered with a layer of cinders, 5 to 6 inches deep, which serves as a kind of filter for the lead.

Softening Hard Lead.—As previously mentioned, the lead from various ores and products is more or less impure, which renders it harder than pure lead. The hardness not only depends on the amount of the impurities, but also on the nature of the impurities. These consist chiefly of copper, iron, arsenic, antimony, tin, etc. Such lead requires to be purified, or "softened" as it is termed, so as to fit it for use. The following analyses of impure lead will be instructive :

<div align="center">ANALYSES OF CRUDE LEAD.</div>

Copper,	.	.	.	·12	·22	·89	·15
Iron,	.	.	.	—	·21	—	—
Lead,	.	.	.	98·72	95·70	91·56	78·55
Tin, .	.	.	.	·01	·21	·04	·16
Arsenic, .	.	.	.	·50	—	1·02	·59
Antimony,	.	.	.	·56	3·66	5·63	20·12
Zinc,	.	.	.	·04	—	·62	·42
Sulphur, .	.	.	.	·05	—	·24	—

The operation of softening is conducted in a reverberatory furnace with a low roof, and the bed is fitted with a shallow iron pan. A charge of 8 to 10 tons of lead is melted, and the stream of air passing through the furnace, along with the flame, oxidises the impurities, together with some of the lead; these oxides collect on the top of the metal as a dross, and are skimmed off. This action of oxidising and skimming off is repeated until samples of the metal, on testing, exhibit the required degree of softness and malleability. The dross, which has a dull brown colour and is hard and heavy, is afterwards reduced for the recovery of the lead.

A process due to Keith, for refining lead by electrolysis, is said to have been in use at New York for some years. The anodes of the electrolysing cells are made of the furnace lead, which is cast in thin plates about 4 feet long and weighing 45 lbs. ; these are enclosed in muslin bags, which serve to retain the gold and silver and other insoluble matters. The cathodes are plates of pure lead, and are placed about 2 inches from the anodes in a bath consisting of a solution of lead sulphate in sodium acetate. The bath is heated by steam to about 38° C., and the electricity supplied by a Weston

<div align="center">T</div>

dynamo working at 1500 revolutions per minute. When the electric current is passed through such a series of cells, the anodes are attacked and dissolved, an equivalent amount of lead being precipitated on the cathodes as a loose crystalline powder, which falls to the bottom of the cell, whilst the matters formed by the disintegration of the anodes are collected in the muslin bags. The action is continued until only 2 or 3 per cent. of the lead forming the anodes remains undissolved. In a series of forty-eight decomposing cells, each containing fifty anodes, 10 tons of 180-ounce silver-lead, with $2\frac{1}{4}$ per cent. of antimony and arsenic, can be refined daily by a 12-horse-power steam engine. The precipitated lead contains 11 grains of silver per ton, and is compressed by hydraulic pressure before melting.*

* Thorpe's *Dict. of App. Chem.*, Vol. II., p. 434.

CHAPTER XIX.

COPPER.

COPPER has been known from the earliest times, and this may be accounted for by the abundance in which it is distributed over the earth, occurring almost as widely as iron, although less plentifully. The ease with which its oxides are reduced and the occurrence of the metal in many parts in the metallic state, together with its colour and other valuable physical properties, especially that of hardness when alloyed with other metals, such as tin, would be most likely to attract the attention of primitive nations, and thus lead to its employment for weapons, tools and agricultural implements, even before the era of iron. The Latin word *aes* in ancient writings sometimes signified copper and sometimes an alloy of that metal, so that probably the metal and those of its alloys which have a reddish colour were confounded together.

Copper has a red colour and brilliant lustre ; it is highly malleable and ductile, so that it may be rolled into very thin sheets and drawn into fine wire. By these and other mechanical operations the metal becomes hard, but its softness may be restored by annealing, and it is immaterial whether it is cooled rapidly or slowly. At temperatures near its melting point it is very brittle, and may be readily powdered. Copper is malleable at a red heat, but at a bright red and at a black heat it is brittle. The tenacity of copper is about 8 tons per square inch. It melts at a temperature of 1050° C., and is not sensibly volatile, except at very high temperatures. Its specific gravity is 8·82, which may be slightly increased, by hammering and rolling, to about 8·90. Copper, when cooled from fusion in contact with the air, is very apt to assume a

vesicular structure, by which its density is greatly diminished. This is doubtless due to the readiness with which the metal occludes gases, and, if melted in contact with charcoal, the reduction of any oxide that it may contain will cause the formation of carbonic oxide, and the endeavour of the enclosed gases to escape when the metal is solidifying is the cause of the cavities. It will be evident that the more the cavities are closed up by hammering, etc., the higher will be the specific gravity. The fractured appearance of pure copper is a fine salmon-red colour and finely granular, but after hammering it exhibits a fibrous fracture with a silky lustre. The conductivity of copper is very high, being nearly equal to that of silver, which is the best conductor known. A very slight impurity will reduce the conductivity of copper, but it depends more upon the nature of the impurity than on its amount. Of the impurities likely to be present, bismuth, antimony, arsenic, and nickel are the most injurious; oxide of copper, iron, tin, phosphorus, and manganese also greatly interfere with this property. It is a remarkable fact that silver and gold, each being excellent conductors, and silver, as stated above, is superior to that of copper, yet when alloyed with copper will reduce its conductivity considerably, according to the amount present. The specific heat of copper is ·094 between 0° and 100° C., and its co-efficient of linear expansion is ·000017 for an increase of each degree centigrade. When pure copper is properly melted and cast in an open mould, its surface does not present any ridge or furrow like that of overpoled or underpoled commercial copper. It crystallises in the regular or cubic system in the form of cubes, octahedrons, etc.

Copper may be obtained in the pure state by the electrolysis of solutions of its pure salts, such as the sulphate and chloride, and the conductivity of the pure metal affords an excellent indication of its degree of purity.

Copper is unacted on by dry air at ordinary temperatures, but rapidly oxidises at a red heat. In moist air it acquires a green coating of basic carbonate, and its oxidation is greatly promoted by the presence of acids in the air. Copper unites with oxygen in two proportions, forming cuprous oxide Cu_2O and cupric oxide CuO; the former is also known as the red or sub-oxide, and the latter as the black or protoxide. When a mass of copper is heated in air or oxygen the red oxide is formed, but this is covered with a layer of black oxide where the oxygen has free access. The red oxide is highly basic, and unites with silica to form silicates. Even

if the black oxide is heated with silica, only a silicate of cuprous oxide is formed, thus :

$$2CuO + SiO_2 = Cu_2O,SiO_2 + O$$
$$Cu_2O + SiO_2 = Cu_2O,SiO_2.$$
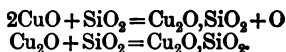
Cuprous oxide is soluble in molten copper, making the fractured surface dry in appearance with a dull red colour, and rendering it brittle in character. This may be removed by re-melting the copper with a little charcoal, and stirring with a piece of wood. The presence of Cu_2O in copper causes the surface of a cast ingot to present a longitudinal furrow, and is known as underpoled copper. The red and brownish red shades on bronzed copper articles are due to cuprous oxide. The black oxide is formed when finely-divided copper is heated in air or oxygen, and is then a black powder ; but when heated to about 1000° C. it evolves oxygen, leaving a mixture of cuprous and cupric oxides $CuO,2Cu_2O$. Both oxides are readily reduced by carbon, carbonic oxide, hydrogen, etc. They both unite with boric acid, forming fusible borates. The black oxide is used to make green and blue glass ; the red oxide is used in making red glass.

Copper and Sulphur unite at a strong red heat, forming cuprous sulphide Cu_2S, which is a dark, bluish-grey, brittle, semi-metallic looking body, with a granular or crystalline fracture. Also when sulphide of iron is strongly heated with oxide of copper, this sulphide is formed and oxide of iron ; if silica is present in addition, a silicate of iron is produced, thus :

$$FeS + Cu_2O = Cu_2S + FeO$$
$$FeO + SiO_2 = FeO,SiO_2.$$
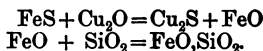
Also, if silicate of copper is fused with sulphide of iron, Cu_2S and silicate of iron are produced. Sulphide and oxide of copper, by the aid of heat, mutually decompose each other, thus : $Cu_2S + 2Cu_2O = 6Cu + SO_2$.

When sulphide of copper is heated alone out of contact with air no change occurs, but in the presence of air or other oxidising agent, such as steam, decomposition occurs. At a moderate temperature the reaction produces copper sulphate, but at a higher temperature this is decomposed with the formation of oxide and liberation of sulphur dioxide. The following equations will show these changes :

$$Cu_2S + 3O = Cu_2O + SO_2.$$
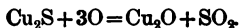
At a bright red heat the following occurs :

$$Cu_2S + OH_2 = Cu_2O + SH_2.$$
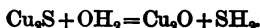
Sulphide of copper unites with other sulphides, such as those of antimony, arsenic, lead, etc., forming complex sulphides. Copper sulphate, or blue vitriol, $CuSO_4$, obtained by the oxidation of copper sulphide ores, is sometimes purposely formed in the extraction of copper and silver. It readily crystallises from its solutions in transparent blue crystals $CuSO_4, 5H_2O$, and has considerable commercial applications, such as in printing and dyeing, and in agriculture.

Copper and Carbon do not unite ; but when copper containing any dissolved oxide is heated with carbon the oxide is reduced, and if any other impurities are present the copper will be what is termed overpoled, so that a little cuprous oxide appears to neutralise the ill effects of these impurities, which would otherwise make the copper brittle.

Copper and Phosphorus unite directly when heated together, and copper containing this element up to about 11 per cent., known as phosphor copper, is largely used for making phosphor bronze and otherwise introducing small quantities of phosphorus into copper alloys. One half per cent. of phosphorus makes copper very hot-short, but a very small quantity may be used to produce sound castings in copper. The 11 per cent. alloy is very hard, of a steel-grey colour, and is susceptible of a high polish, but tarnishes very readily. Phosphor copper may be prepared : (1) By dropping phosphorus upon molten copper in a crucible an alloy rich in phosphorus is obtained, forming an extremely hard, steel-grey, fusible compound. (2) By reducing phosphate of copper with charcoal, or charcoal and carbonate of soda. (3) By heating a mixture of 4 parts bone ash, 1 part charcoal, and 2 parts granulated copper at a moderate temperature. The melted phosphide of copper separates on the bottom of the crucible, and is stated to contain 14 per cent. of phosphorus. (4) By adding phosphorus to copper-sulphate solution and boiling. The precipitate is dried, melted, and cast into ingots. When of good quality and in proper condition it is quite black. (5) Copper phosphide is easily prepared by adding to a crucible 14 parts sand, 18 parts bone ash, 4 parts powdered coal, 4 parts sodium carbonate, and 4 parts powdered glass ; the whole being intimately mixed with 9 parts granulated copper. A lid is then luted on, and the crucible exposed to a strong heat. The sand acts on the bone ash, forming silicate of lime and phosphoric acid. The

liberated phosphoric acid is reduced by the coal, and some of the phosphorus thus set free unites with the copper.

Name.	Composition.	Colour.	Streak.	Hardness.	Density.
Cuprite, ...	Cu_2O	Red	Brown-red	$3\frac{1}{2}$–4	5·7–6
Melaconite, . . .	CuO	Black	Black	—	—
Malachite, . . .	$CuCO_3,CuH_2O_2$	Green	Green	$3\frac{1}{2}$–4	3·7–4·1
Azurite, . .	$2CuCO_3,CuH_2O_2$	Blue	Blue	$3\frac{1}{2}$–4	3·5–3·8
Copper pyrites (yellow copper ore),	Cu_2S,Fe_2S_3	Yellow	Black	$3\frac{1}{2}$–4	4·1–4·3
Bornite (purple copper ore),	$3Cu_2S,Fe_2S_3$	Variegated	Black	3	4·9–5·1
Fahlore (grey copper ore),	Mixed sulphides of $Cu,Sb,AsFe$	Grey	Black	3–4	4·3–5·4
Copper glance, .	Cu_2S	Lead-grey	Lead-grey	$2\frac{1}{2}$–3	4·8–5·8

(6) Montefiori-Levi and Künzel prepare phosphor copper by putting sticks of phosphorus into crucibles containing

molten copper. To avoid a too ready combustion the sticks of phosphorus are previously coated with a firm layer of copper, by placing them in a solution of copper sulphate. (7) By strongly heating in a crucible an intimate mixture of bone ash, copper oxide, and charcoal, phosphor-copper is produced.

Copper and Silicon unite when silica and silicon compounds are reduced in presence of copper. Silicon increases the hardness and impairs the malleability of copper. With 4·5 per cent. the copper has a bronze colour, and with 12 per cent. it is white. It is used in silicon bronze. (See Chapter on Alloys.)

Impurities in Copper.—Arsenic, silver, sulphur, and oxygen are generally present, and frequently iron, antimony, bismuth, tin, lead, nickel, cobalt, and gold. The general effect of these elements is to harden and impair the conductivity and ductility. Bismuth is very injurious, even in minute quantities.

ORES OF COPPER.

Native copper occurs in the Lake Superior region and at Santa Rita, New Mexico ; in Brazil, Chili, Peru ; in Cornwall and in North Wales ; but the supply of copper from this source is very limited compared with that obtained from other ores. The native copper occurs in masses and in fine grains in sand. Sometimes the earthy matter exceeds 99 per cent., but this is easily removed by mechanical means. Native copper is often covered with an incrustation, more or less thick, of oxide and carbonate, and often contains silver and other metals alloyed with it. The chief ores of copper may be summarised according to table on preceding page.

Chrysocolla, a hydrated silicate, as well as phosphates, sulphates, etc., are occasionally found and used as ores of copper. Pyrites largely occur with only small quantities of copper. Analyses of certain samples of copper ores are given in annexed table, to give a general idea of their composition, which, of course. varies considerably.

METHODS OF EXTRACTION.

These may be classified in two main divisions : (1) dry methods, involving fusion ; (2) wet methods, including electro-chemical processes. Of the former, we may subdivide them

TYPICAL SAMPLES OF COPPER ORES.

NAME	Native Copper		Red Oxide	Malachite	Azurite	Grey Sulphide	Purple Copper	Fahlers or Grey Copper Ore		Chrysocolla	Atacamite	Pyrites	
LOCALITY	Lake Superior	Brazil		Siberia	Chessy	Cornwall	Cornwall	Harz	Cornwall	Lake Superior	Copiapó	Cornwall	Cornwall
ANALYST	Hautefeuille		Chenevix	Klaproth	Phillips	Thompson	Pulsnet	Rammelsberg	Phillips	Rammelsberg	Field	Phillips	Varrentrapp
Cu,	69·28	99·46	88·78	71·7	69·08	77·16	56·76	30·47	47·7	42·32	70·74	30·0	58·2
CuO,													
Fe,		·1				1·15	14·84	3·52	9·75			32·2	14·84
Ag,	5·45	·3						10·48					
Au,		·08											
S,						21·62	28·24	24·8	30·25			35·16	26·96
H_2O,				7·8	5·46					20·68	17·79		
O,			11·2										
CO_2,				20·5	25·46								
Cl,											11·44		
Fe_2O_3,										1·63			
Cu,										1·76			
MgO,										1·06			
Zn,								3·39					
Pb,								·78					
Sb,								26·56					
As,									12·26				
Hg,													
SiO_2,	·019									32·55		2·64	
Gangue,	25·24												

Fig. 119.

according to the type of furnace usually employed, viz., the reverberatory furnace or reaction method, and the blast furnace or reduction method.

1. ROASTING AND REACTION IN REVERBERATORY FURNACES.

Pyritic ores form the base of the materials employed, but oxides and carbonates are frequently added. It is sometimes termed the Welsh method, being very largely conducted at Swansea, in South Wales. The following are the principles involved : (1) When sulphides of iron and copper are roasted in air, a portion of the sulphur is oxidised, forming sulphur dioxide, and some of the iron and copper is also oxidised ; but on fusing the mass, the oxide of copper reacts on the unaltered sulphide of iron, forming more oxide of iron, and converting the copper oxide into sulphide, because copper has a greater affinity than iron for sulphur. (2) When oxides and sulphides of iron or copper are fused with silica a fusible silicate of the oxide is formed, but the sulphide is not affected. (3) When sulphides and oxides of copper are fused together, the sulphur combines with the oxygen, and the copper is reduced to the metallic state. (4) When a silicate of copper is fused with sulphide of iron or pyrites, the copper leaves the silicate and combines with the sulphur, and the iron takes the place of the copper in the silicate, forming sili ate of iron. These reactions may be expressed by the following equations :

$$
\begin{cases}
\text{Cu}_2\text{S} + \text{FeS} + \text{O} = \text{Cu}_2\text{O} + \text{FeO} * \\
\text{Cu}_2\text{O} + \text{FeS} = \text{Cu}_2\text{S} + \text{FeO} \\
2\text{Cu O} + 2\text{FeS} = \text{Cu}_2\text{S} + 2\text{FeO} + \text{S}
\end{cases}
$$
$$2. \quad \text{FeO} + \text{SiO}_2 = \text{FeO,SiO}_2$$
$$3. \quad \text{Cu}_2\text{S} + 2\text{Cu}_2\text{O} = 6\text{Cu} + \text{SO}_2$$
$$4. \quad \text{Cu}_2\text{O,SiO}_2 + \text{FeS} = \text{FeO,SiO}_2 + \text{Cu}_2\text{S}.$$
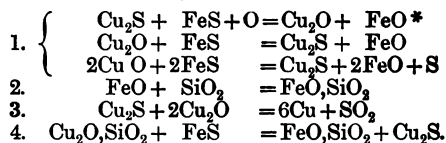
In the Welsh method of smelting pyrites, the number of operations may be considerably diminished by the judicious use of oxidised ores, added to the furnace charges at different stages of the process, since these oxidised compounds react according to the above equations, and greatly assist in the removal of the sulphur, as well as serve as a source of copper. The process, as conducted in six stages, is shown in the annexed scheme (Fig. 119).

1. **Calcination with Air.**—Volatile matter, such as arsenic, water, carbonic acid, sulphurous acid, etc., is expelled,

---

* This is not a complete equation, as the change is only partial.

some iron is oxidised, and the product contains iron, copper, silicon, sulphur, oxygen, and earthy matter. In those cases in which arsenic and antimony are present, the calcination requires great care in order to effect the removal of these impurities without loss of copper. This may be done by regulating the supply of air, so as to sublime the sulphides of these metals. Or the ore may be cautiously oxidised by air, and fine coal added to decompose the arseniates and antimoniates produced by the oxidation. Another plan is to roast the ore "sweeter" than usual, *i.e.*, to carry the operation further in order to remove much more of the sulphur; so that when the mass is fused in the next stage there is insufficient sulphur to unite with the copper, and reaction ensues between some of the sulphide and the residual oxide of copper, with formation of metallic copper. Such copper is very impure, as it then contains much of the arsenic, antimony, and any gold, silver, etc., that may be present.

Calcination, or roasting, is conducted in heaps, stalls, kilns, and reverberatory furnaces. Heap roasting is more largely used in connection with the reduction method in blast furnaces than in the reaction method in reverberatory furnaces. The ore is broken into lumps of suitable size and piled up in a heap on a carefully prepared and raised foundation of stones, slag, etc., faced with clay. Fine ore is first laid on about 6 inches deep, then logs of wood to a depth of 12 inches, and on this the ore in small lumps. The whole is covered over with fine ore, so as to exclude the free admission of air. Suitable vents are left in the wood, which communicate with the central chimney, which is formed of boards roughly nailed together. Other vents are opened at intervals. Such a heap may contain 250 tons of material, and be about 40 feet long, 50 feet wide, and 6 feet high. The ore will probably require seventy to eighty days for its complete calcination. The height of the heap is important, as a high heap means a higher temperature than a low one, and the charge may get so hot as to clot together and hinder the calcination. The greater the percentage of sulphur in the ore the lower should be the heap, as the heat required for the process is obtained by the oxidation of the sulphur.

Stalls are simply spaces for calcination, surrounded by walls, a common size being 9 feet long, 7 feet wide, and 6 feet high. They are generally built back to back, and a row of several stalls is placed in a line. The walls contain central flues which communicate with a chimney, or the flues may conduct the gases to a sulphuric acid chamber. The charging

and arrangement are similar to that of heaps, but the heat is better concentrated, and the duration of the operation shorter.

Kilns are used for ores poor in sulphur. They resemble ordinary shaft furnaces, but the zone of combustion is greatly extended, since the temperature required is very moderate. The Gerstenhoffer calciner (Figs. 120, 120A) is a rectangular kiln 20 feet high and 5 feet across, in which are arranged 20 rows of triangular fire-clay bars, 2 feet 6 inches long.
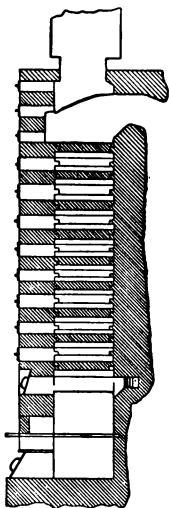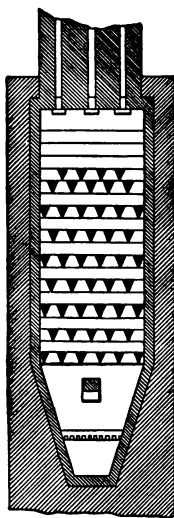
Fig. 120.   Fig. 120A.

The ore is ground fine, and the supply, regulated by feed rollers, passes through three narrow channels, and falls on the flat surface of the bars, then gradually descends as fresh ore is added, being oxidised in its descent, and is finally removed at the bottom. Air is admitted by a series of apertures in the front of the furnace, and the combustion of the sulphur maintains the necessary temperature. If rich ores were treated in this kiln, they, being more easily fusible, would clot together on the bars and choke the draught, as well as defeat the object of the calcination.

Reverberatory furnaces are used for rich ores in a somewhat finely divided state. They generally have a long bed and comparatively small fire-place; the roof is low and contains two or more hoppers for charging, according to the size. An old form still in use for calcining 3 or 4 tons is shown in Fig. 121. It is lined with fire-brick, the bed being from 16 to 25 feet long and 12 to 14 feet wide. Several attempts have been made to utilise the sulphur given off during calcination. Mr. Spence invented a furnace for this purpose, 50 feet long, heated from beneath, so that the furnace contains two chambers—an upper one in which the ore is placed, and a lower one through which the products of combustion pass. The sulphur liberated from the ore in
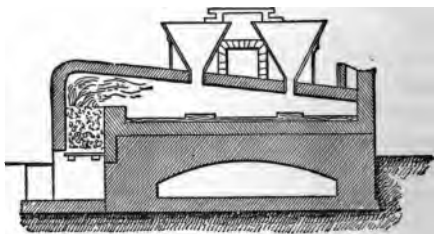
Fig. 121.

the form of SO_2 is utilised for the manufacture of sulphuric acid (see Fig. 109).

Revolving cylinders are now being largely used for calcining copper ores and mattes similar to those employed for the chlorinising roasting of gold and silver ores. The Brückner cylinder is one of the best forms of this type. It is made about 18 feet long and 8 feet wide, and lined with fire-brick. A double feed hopper is fixed above the furnace, which has two sets of holes on opposite sides for facilitating the discharging of the roasted ore. The fire chamber is really a car running on a track at right angles to the major axis of the cylinder, and having a flue that comes exactly opposite the throat of the furnace. In this way the heat may be generated for starting the combustion of the sulphur, and when this is well kindled, the fire box may be removed, the flue door closed, and the roasting allowed to go on while the cylinder is being revolved. One fire box will suffice for several cylinders, but it is necessary to re-connect

the fire box to complete the calcination when the sulphur has been nearly consumed. The general shape of the Brückner cylinder is shown in Fig. 94.

Kernel Roasting.—This is an ancient process, formerly conducted in many parts of Europe, and now said to be carried out at Agordo in the Venetian Alps, the ore having an average composition of 2 per cent. of copper. It is a cupriferous iron pyrites and when roasted in lumps, 2 to 3 inches square, the copper becomes concentrated in the centre, forming a nucleus consisting essentially of copper, iron, and sulphur and containing 4 to 5 per cent. of copper. The outer shell consists chiefly of oxide of iron, with a little copper oxide and some copper sulphate, which latter is dissolved out with water.

The calcination was conducted originally in heaps, but was afterwards performed in kilns. The kiln (Fig. 122) is a rectangular chamber within four walls divided into sections.
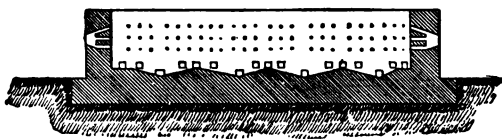
Fig. 122.

The bed of each section is made in the form of a pyramid, on the top of which a chimney is roughly built with pieces of ore, and the spaces between are filled with the ore to be roasted. The kernels obtained are smelted by the blast furnace method to obtain metallic copper. The gases evolved from copper calciners are very injurious, and consist chiefly of nitrogen, carbon and sulphur dioxides, and some free oxygen.

2. **Fusion for Coarse Metal.**—The charge consists of calcined ore, metal slag and a little fluor spar. The products are a regulus of copper and iron, termed coarse metal, and an acid silicate, chiefly of iron (FeO,SiO_2) containing some of the impurities. The amount of copper in this slag is generally less than 2 per cent., so that it is considered "clean," and therefore thrown away. In order to avoid loss of copper by the fluxing of the oxide of copper produced during roasting, fresh sulphide ore is added, and this reacts on the oxide, producing sulphide of copper and oxide of iron, as seen in the foregoing equations. Coarse metal is a bronze-

coloured, strong-looking, brittle and porous mass containing
about 30 per cent. of copper and an equal quantity of iron.
The slag is a dark-coloured brittle substance, often containing
bits of quartz and globules of coarse metal. Regulus and
slag are tapped into sand moulds.

The melting furnace has a smaller bed and larger fire-place
than the calciner. The ratio of the area of the grate to that
of the volume of the laboratory is as 1 : 5 or 6. Fig. 123
shows a section of an ore-melting furnace. The bed or
laboratory is an oval chamber, lined with sand and metal
slag, 13 feet × 9 feet, shaped hollow and inclining from all
parts to the tap hole. The fire-bridge is generally hollow, to
allow for the passage of air to keep it cool, and the roof is
pierced with one opening communicating with the charging
hopper.
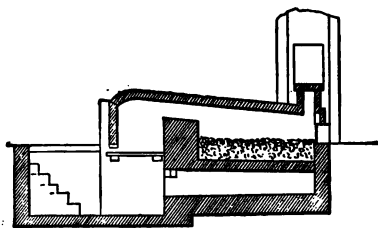
Fig. 123.

3. Calcination of Coarse Metal (termed regulus or
matte).—This operation is very similar to that of ore calcina-
tion, and the matte requires to be finely ground. The
product is a black friable mass, and the effect of the cal-
cination is to remove more of the sulphur and oxidise more
of the iron and copper.

4. Fusion for Blue, White, or Pimple Metal.—The
product of No. 3 is melted in the furnace (Fig. 123) with
roaster and refinery slags, and a certain proportion of
oxidised ores, such as oxides and carbonates, which react on
the regulus and shorten the operation, the object being to
convert the whole of the iron sulphide into oxide, leaving the
copper as sulphide. When the oxidised ore is insufficient,
blue metal results, which contains sulphide of iron ; when
just sufficient, white metal, which is sulphide of copper,
results ; when in excess, some of the sulphide of copper is
reduced, and the surface of the metal has a number of

pimples due to the attempt of sulphur dioxide to escape. It is then termed pimple metal.

Blue metal is a brittle substance with an uneven fracture, of a purplish-blue colour when broken hot, and a bronzy tint when broken cold, and contains about 56 per cent. of copper. It is often covered with fine strings of nearly pure metallic copper called "moss" copper, produced by the reaction of sulphide on oxide of copper, and soluble in the molten regulus.

White metal is compact, brittle, with an uneven granular or crystalline fracture, and of a bluish-grey colour. It contains about 77 per cent. of copper.

The slag is compact, brittle, with an uneven fracture, leaving sharp edges; granular and sometimes crystalline, of a dark bluish-grey colour, with cavities on the surface. It is termed metal slag, and is basic in character.

5. This stage is termed, by copper smelters, "roasting." It consists of roasting the matte, produced in the previous process, in a furnace similar to that used for making coarse metal, until sufficient of the sulphide of copper is oxidised, then raising the temperature to the fusing point of the charge, when the oxide reacts on the unaltered sulphide, producing an impure copper, termed "blister copper," and a rich slag, termed "roaster slag," which is either added to a charge in the fourth stage, or treated by itself, if very impure, for the extraction of the copper. The surface of the ingot is covered with blisters, due to the escape of sulphur dioxide after the metal has partly solidified on the surface. The slag is sometimes light, porous, and of a black colour, sometimes dense and close, containing shots of copper, and of a reddish-brown or black colour.

6. **Refining Blister Copper.**—The blister copper is charged on to the bed of a reverberatory furnace having a larger proportion of grate area than in the preceding melting furnace. The volume of the laboratory is 158 cubic feet and the section of fire-place is 19 square feet. It has no charging hopper and no side tap hole. The bed slopes from all parts towards the dished portion, in which the metal collects. The charge is about 10 tons. The cakes of copper are arranged in a hollow pile and gradually melted in an oxidising atmosphere, which takes about five hours. During this time the impurities are largely oxidised, and some of the volatile ones volatilised, such as sulphur, arsenic, and antimony. The remaining oxides unite with silica to form a fusible slag or scoria, which is very rich in oxide of

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copper and therefore highly basic. The copper still retains some impurities and red oxide of copper. These are removed by covering the metal with anthracite powder and inserting a pole of green wood which produces reducing gases, such as CO and CH$_4$, which act chemically in reducing oxide of copper, and mechanically in bringing the impurities to the surface. If the poling is insufficient the copper is dry in appearance, dull in lustre, and cracks at the edges when hammered, and is then termed "underpoled" or dry copper. When the right degree of poling is effected it is said to be at tough pitch. If the poling be carried too far the copper loses its malleability and ductility. This is probably due to the reduction of the oxides of foreign metals, such as lead and antimony, which alloy with the copper. Overpoling may be remedied by admitting a little air to the copper. An ingot of overpoled copper has a longitudinal ridge on its surface and underpoled copper has a longitudinal depression, while tough copper has neither ridge nor furrow, but a level surface. The refined metal so obtained is not pure, but the bad effect of the impurities is neutralised by the presence of about ·25 per cent. of oxygen. In the refining process, use is sometimes made of the fact that if one readily oxidisable element is present it induces other less oxidisable elements to combine more rapidly with oxygen at the same time; phosphorus and lead have been added in some cases for this purpose, but a little of these elements remain and injure the copper, so that these elements cannot be used when copper of a high degree of purity is desired.

Best Select Process.—The best varieties of commercial copper are known as best selected. The following method is sometimes resorted to in producing this high grade copper, depending on the following principles. When an impure regulus, consisting largely of white or pimple metal, is tapped from a furnace, the portions which are first run out, and which occupied the bottom position in the furnace, are found to be the most impure, and when gold and silver are present, these metals are found in these first tappings. The portion which is last tapped is therefore the most pure and is employed for the production of best select copper, while the impure regulus yields on reduction a crude metal termed "bottoms" or tile copper. Or the impure regulus may be melted and cast a second time, when the impurities will be still further concentrated in the ingots which are first tapped. Another method is to carry the oxidising roasting of the raw regulus further than in the ordinary process, so

that, when the charge in the fourth stage is melted, the excess of oxide reacts on the sulphide and produces metallic copper, which, when tapped, being specifically heavier than the regulus, sinks to the bottom, and the regulus rises to the top of the ingot. The copper reduced at this stage is very impure, and contains any gold, silver, etc., that may be present. This method is largely used for extracting such gold from copper by means of "bottoms" (see Fig. 119).

Mr. Vivian (Sir Hussey), in 1851, took out a patent for separating nickel and cobalt from copper ores by means of bottoms. He proposed to convert the nickel into speise by means of arsenic, and the copper into regulus by means of sulphur. When such a mixture is tapped out, the speise sinks to the bottom and the regulus occupies the upper position, and, being brittle, may be detached from each other when cold. The speise contains much copper, so that the operation has to be repeated a second or third time.

2. REDUCTION PROCESS IN BLAST FURNACES.

This method was previously adopted where fuel was dear, the ores poor, refractory, and not too complex; but in America this system has been very largely employed for almost all classes of ores. The American ores as a rule are purer than European ores. At any rate a very large supply of such ores is available to the smelter, both in the oxidised condition and as complex sulphides. The following method as formerly carried out in Sweden may be taken as a type :

1. The ore is roasted in heaps, 30 ft. square and 12 ft. high, or in stalls which are composed of three walls ; the burning of the sulphur, together with some wood, maintains the heat.

2. The calcined ore is then melted in the blast furnace (Fig. 124) with slags obtained from the black copper in No. 4. The furnace is 18 ft. high, 3 ft. 10 ins. wide at the twyers, and the hearth is 5 ft. 4 ins. deep. In from two to three days the hearth is filled with regulus containing about 30 per cent. of copper, which is tapped into sand moulds.
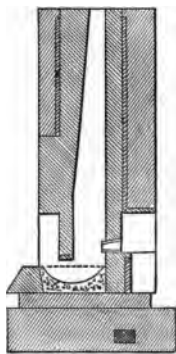
Fig. 124.

3. Roasting the regulus from No. 2 called raw "matt." This is conducted in heaps, 11 ft. × 5 ft. × 5 ft. high, each heap containing about 5 tons of matt, and requiring seven to eight weeks for completion.

4. Smelting for black copper.—The roasted regulus is rich in metallic oxides and requires a siliceous flux, such as ore slag. The charge consists of 2 cwts. calcined regulus, 28 lbs. of copper residues, 28 lbs. of ore slag, 12 lbs. of quartz, and 18 lbs. of charcoal. One operation lasts from two to three days, and the products are—black copper containing about 94 per cent. of copper, a regulus containing 60 to 70 per cent. copper, and a slag composed chiefly of silicate of iron (FeO,SiO_2). The furnace is represented in Fig. 125.
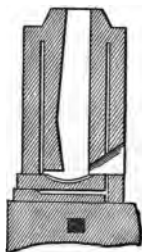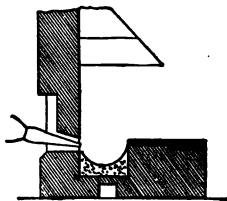
Fig. 125.   Fig. 126.

5. Refining black copper.—The refining is conducted in the blast hearth (Fig. 126), $2\frac{1}{2}$ ft. × 2 ft. diameter, and 15 to 18 in. deep, lined with fire-clay and sand. The twyer inclines at an angle of 45°. The copper is melted with charcoal by the aid of a blast of air and the bath of metal kept covered with charcoal during refining. The slag is removed two or three times, and when it becomes red from the presence of oxide of copper the blast is turned off, the charcoal pushed back, and the slag solidified by projecting water on to the surface, and then removing it as a cake. The copper is kept covered with charcoal until sufficiently refined or until the excess of cuprous oxide has been reduced by the carbon.

The operations in the blast furnace method are theoretically identical with the reverberatory method until the production of blue or white metal is obtained. These mattes are roasted completely to oxide and then reduced by carbon. By this process a considerable quantity of copper oxide

necessarily passes into the slag in order to flux off the impurities, and the reduced copper is liable to be very impure if certain impure ores are used.

A modern American furnace is shown in Fig. 127, known as the Herreshoff furnace. The body consists of a double iron casing through which water is made to circulate in order to keep it sufficiently cool, and is supported on four iron pillars. The bottom plate is lined with fire-clay, well rammed in, or with fire-brick resting on a layer of sand. A
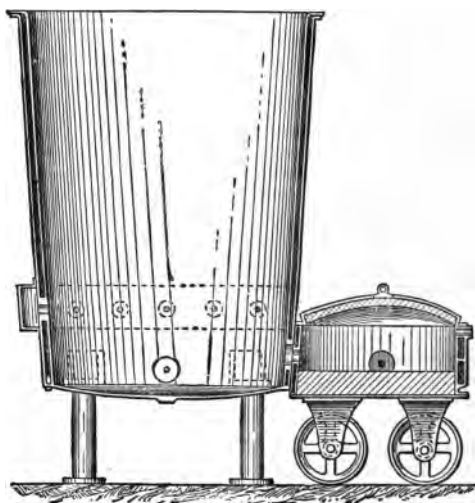
Fig. 127.

wind chest for admission of the cold blast to the twyers is fixed on one side. The cooling water enters at one side and makes its exit at the other. The furnace is charged from the top, which is covered with a hood connected with a lateral pipe to carry away the waste gases. The fore hearth lined with fire-brick is detachable and mounted on wheels. It has an opening in the lateral wall which communicates with the interior of the furnace. The slag is removed by means of a lip at the front of the fore hearth, and the regulus or metal is run off through a tap hole at the bottom.

The furnace is rectangular in shape with rounded corners, 10 feet high, 3 feet 7 inches × 6 feet 4 inches at the bottom, and 4 feet 7 inches × 7 feet 4 inches at the top. The water jacket has a space of only 2 inches, but this is exceptionally small. The diameter of the twyers is 4 inches, and the pressure of the blast ¾ lb. per square inch.

The raw copper obtained from the blast furnace is refined in a reverberatory furnace. When gold and silver are present, which is not uncommon in American ores, the copper is specially treated for their extraction, and the copper is largely obtained by electro-deposition. When pigs of copper have to be refined, they retain their shape until the fusing point is reached, when they soften and melt suddenly, and then the impurities are oxidised with the formation of much oxide of copper, which also acts as an oxidiser for base metals. A thin slag forms on the surface and is removed at intervals. This gradually gets more basic as the process proceeds, and as the sulphur is removed the escape of gas ceases. The charge is then constantly rabbled for about two hours, when the copper gradually becomes "dry," in consequence of the dissolved oxide, and has a brick-red colour when cold. The operation of poling, which lasts about one hour, is then commenced, the surface of the metal being covered with charcoal, and when a test sample shows no contraction or depression on cooling, and the structure of a broken piece is fibrous and silky with a rose-red colour, the refining is complete.*

Basic lined furnaces for roaster and refinery furnaces have been tried. Gilchrist † in 1891 added arsenical copper in varying amounts to slag and regulus in a furnace lined with prepared dolomite. The mixture was so regulated that there was insufficient sulphur to combine with all the copper, and by a quick fusion a considerable quantity of regulus nearly free from arsenic was obtained and a small quantity of very impure copper as "bottoms." An average analysis of these bottoms gave:

Copper,	.	.	.	.	.	83 to 87
Arsenic,	.	.	.	.	.	5 to 7
Sulphur,	.	.	.	.	.	1 to 3
Iron, .	.	.	.	.	.	·5
Lead, .	.	.	.	.	.	3 to 5
Silver,	.	.	.	.	.	·5

It is to this impure copper that the basic method is particu-

* Peters' *Copper Smelting*, p. 285.
† *Jour. of Soc. of Chem. Indus.*, 1891.

larly applicable. A basic lining favours the removal of arsenic from copper.

The blast furnace is specially adapted to highly ferruginous ores in places where anthracite, coke, etc., is dear, and is very suitable for oxidised and low grade native copper. The reverberatory method is advantageous : (1) for highly refractory siliceous, aluminous, and calcareous ores; (2) where mixed and varied ores only are attainable; (3) where anthracite and similar fuels are cheap ; (4) for smelting rich native copper.

Bessemer Converter.—This vessel has been applied to copper smelting, and what is known as the Manhès' process seems to be the most successful. The regulus is run into the converter in the molten condition and air blown through the mass. Iron and other impurities as well as some of the copper are oxidised and at once act on the furnace lining, forming a slag, and leaving a rich copper regulus. The slag is then removed and the blow continued until the sulphur is burnt off, the combustion of which furnishes the necessary heat. The great difficulties are the small amount of heat produced by the burning of the sulphur, and the tendency of the metal to choke the twyers. They were therefore placed at the side and the effect of side blowing tried. It was even then found that the lining was rapidly scorified by the metallic oxides, so that a more or less basic lining had to be adopted. The blow lasts 20 to 25 minutes for white metal, which is converted into blister copper. For blue metal two blows are usual. The latest form of converter is a horizontal one, turning on axial trunnions, and through one of these the blast passes to the row of twyers parallel to the axis. The twyers are so arranged as to allow of their alteration in level during the blow. This enables the blast to pass only through the unreduced regulus, and avoids the necessity of sending air through the reduced copper at the bottom of the vessel.

The Bessemer process has been tried for treating a mixed regulus of copper, nickel, and iron, as obtained from the Sudbury ores in Ontario. According to the chemical affinities of the above metals, the iron should oxidise first, then the nickel, leaving the copper unoxidised, if the process is stopped at the proper stage. When sufficient sulphur is removed, the oxide of iron will unite with silica to form a slag, then some of the nickel may be oxidised and scorified, but the greater proportion of the remaining mixed sulphides will probably be simultaneously reduced by the reaction of

sulphides on oxides, and producing an alloy of copper and nickel which may be separated by electrolysis. The method is still in the experimental stage.

WET METHODS OF EXTRACTION.

Generally where the ores are poor in copper and fuel expensive, wet methods are best. In some cases copper pyrites, by the action of air and moisture, is converted into copper sulphate, which is dissolved by water, forming a solution from which the copper is precipitated by iron, thus:

$$CuSO_4 + Fe = FeSO_4 + Cu.$$
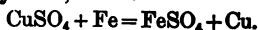
One of the most successful methods is due to Henderson and largely carried out by the Tharsis Company, but its success is due more to extraction of the gold and silver present than to the chemical extraction of the copper alone. The ore is first roasted to remove the greater part of the sulphur for the manufacture of sulphuric acid, leaving the iron as oxide and sulphur in about equal amount to that of the copper present. The ore contains 2 to 3 per cent. copper and small quantities of silver and gold, which are recovered by the Claudet process. The mode of procedure may be explained by means of the annexed scheme (Fig. 128).

Fig. 128.

Ore mixed with salt — Ground and Sifted — Hopper — Calciner — Lixiviating Vats — Settling pit — Precipitation of Silver / Copper Chloride Solution — Precipitating Copper — Melting Copper precipitate — Refining Copper — Silver Iodide washed — Silver Precipitated — Drying Silver mud — Assay Room
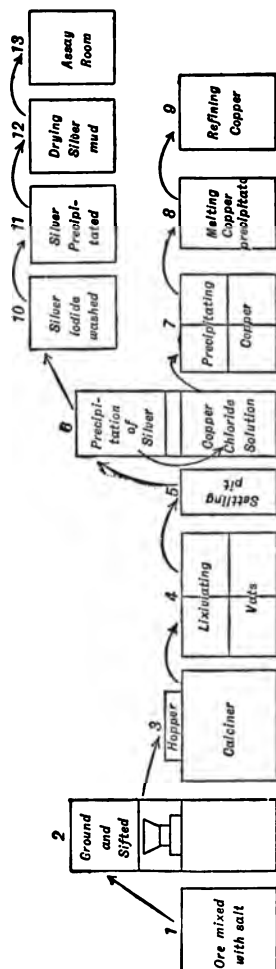
1. the roasted ore is mixed with salt, ground, sifted, and roasted, forming cupric chloride and sodium sulphate, which are dissolved in acid liquors :

$$CuSO_4 + 2NaCl = CuCl_2 + Na_2SO_4.$$
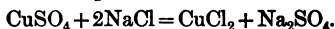
2. The silver in solution is then precipitated by a solution of zinc iodide, and the copper liquor syphoned off, leaving the silver iodide as a powder at the bottom. Care must be taken in the previous processes to keep the copper in the cupric form, as any cuprous salt which may be present is precipitated with the silver as cuprous iodide.

3. The copper chloride solution is run into vats and the copper precipitated by means of scrap iron :

$$CuCl_2 + Fe = FeCl_2 + Cu.$$
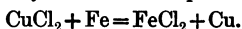
The precipitate is washed, then melted and refined in reverberatory furnaces as in the Welsh method.

4. The silver iodide is washed, and the silver displaced by means of zinc, whereby zinc iodide is reproduced. The chemical changes are shown by the following equations :

$$2AgCl + ZnI_2 = 2AgI + ZnCl_2$$
$$2AgI + Zn = ZnI_2 + Ag_2.$$
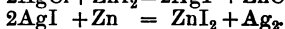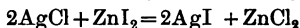
Gold, if present, goes with the silver.

An improvement on the above method is that introduced by Hunt and Douglas, and termed by them the "dichloride process." If the ore is roasted with salt, a chloride of copper is formed, which is dissolved in a solution of ferrous chloride and sodium chloride. When a current of sulphur dioxide is passed into the chloride solution an insoluble cuprous chloride is precipitated with the evolution of hydrochloric acid and the formation of sulphuric acid. The acid liquor when removed from the precipitate is available for dissolving fresh portions of roasted ore. The cuprous chloride held in suspension in acidulated water may be precipitated by iron or decomposed by lime, giving, in the latter case, cuprous oxide and calcium chloride. The copper precipitate is refined, or, in the case of the oxide, reduced and refined in reverberatory furnaces in the usual way. The following equations represent the changes :

$$2CuSO_4 + 2NaCl + SO_2 + 2OH_2 = Cu_2Cl_2 + Na_2SO_4 + 2H_2SO_4$$
$$3CuO + 3Cu_2O + 6FeCl_2 + 3O = 3Cu_2Cl_2 + 3CuCl_2 + 3Fe_2O_3$$
$$Cu_2Cl_2 + Fe = FeCl_2 + 2Cu.$$
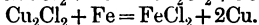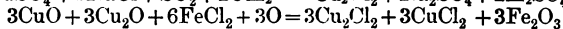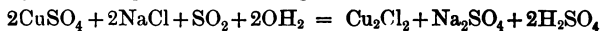
If any silver is present it is left in the residue after the removal of the copper.

ELECTROLYTIC EXTRACTION OF COPPER.

In depositing copper by means of electricity it is necessary that the metal should be in solution, copper sulphate being generally employed. If copper regulus is to be treated, it is cast into flat slabs, rods of copper being placed in for supports and connections; these slabs form the anodes in solutions of copper sulphate. The current is obtained from a dynamo machine. The electrolytic process is chiefly employed in refining pure copper, and is specially applicable to copper "bottoms" containing gold and silver.

The impurities, especially arsenic, antimony, and bismuth, introduce many difficulties in the way of successful working, and great experience is required to overcome them. The principle of the process rests on the fact that when the anode or the solution contains several metals, the current makes a selection, and deposits them in a definite order.

That metal will be first dissolved from the anode, the solution of which causes the development of the greatest amount of energy, and that metal will be first deposited from solution, the separation of which requires the least consumption of energy. Thus, suppose the following metals present in the anode—zinc, iron, tin, nickel, lead, arsenic, bismuth, antimony, copper, silver, and gold. All those which precede copper will be dissolved first, and those which follow copper will be dissolved last. When the above metals are in solution, the gold will be the first to be deposited and the zinc the last. But this rule is dependent on the strength of current, nature of solution, whether acid or alkaline, and the proportions of the constituent metals. If the current exceeds a certain strength all may be dissolved and deposited together, and the more neutral the solution the more easily will the electro-negative metals be dissolved, and the more easily will the electro-positive metals be deposited. If a copper anode contains a large amount of impurities, these will be more readily dissolved than from copper containing only a small amount. The less dense and compact the anode is, the better will the process go on.

The foregoing remarks apply to copper containing metals in the metallic form. If they are present as oxides or sulphides, the former, being chiefly non-conductors, simply fall to the bottom of the vessel, the latter, being conductors, may be dissolved and the metal deposited; but if there is much copper in the anode and little sulphide, the latter falls to the bottom and the copper only is deposited.

Electro-deposited copper, from a copper chloride or sulphate solution, is remarkably pure, for silver and gold, when present, are precipitated from the solution; lead forms an insoluble sulphate; iron, zinc, and tin are too electro-positive to be deposited at the same time as copper, and the same applies to nickel, although in a less degree. The greatest danger is with antimony and bismuth, when those metals are present in solution with the copper.

The vats employed for the deposition of copper are made of wood, lined with lead or sometimes coated with pitch. The size of the vat varies greatly, but 3 feet 6×4 feet $\times 4$ feet deep will answer very well. Each tank is roughly insulated by standing on wooden tressles. At one of the sides of the tank are the two main conductors, and cross bars from these support the anodes and cathodes, each set being insulated from the other set. Impure slabs of copper are suspended from the anodes, and thin sheets of pure copper, on to which the electrolysed copper is deposited, form the cathodes. The distance of anode from cathode is about 2 inches, but this depends on the strength of current and purity of the copper.

The bath consists of a solution of copper sulphate containing about $\frac{1}{2}$ lb. of sulphuric acid and 2 lbs. of copper sulphate per gallon. For regular deposition the solution must be kept in motion, and yet allow the slimy mud to settle properly to the bottom. The tanks being arranged in tandem fashion in a gradual descending series, a syphon pump causes the liquid to flow from the bottom of one tank to the surface of the next, and so on. A current of considerable electro-motive force is employed, and the tanks connected in series. Mr. Hartmann some years ago took out a patent for the prevention of "polarisation" of the electrolyte when copper is being precipitated by electrolysis from a solution of sulphate of copper, using insoluble anodes. He introduces sulphur dioxide into the liquor, which is at the same time warmed either by taking the gas direct and hot from kilns, or calcining furnaces, or by passing steam in lead coils. The baths are covered with well-fitting covers, which have pipes leading from them to carry off the excess of sulphurous acid gas. By this employment of sulphur dioxide the oxygen liberated at the anodes is at once absorbed and neutralised, combining with the sulphurous acid to form sulphuric acid. The free acid so produced helps to keep the bath in good order as regards conductivity, till nearly all the copper is removed.

In the Siemens process of extracting copper from ores, which was commenced at Martini, Berlin, in 1890, the chief difficulty attending the electrolytic method of extracting copper has been overcome by adding to the decomposing copper-carrying solution another solution, which takes up the oxygen set free at the insoluble anode and succeeds in lessening the polarisation. For the deoxidising solution, ferrous sulphate is employed. This substance is changed by the oxygen set free at the anode into ferric sulphate. In this way a lixiviant for the copper contained in the ore is obtained, for ferric sulphate will dissolve metallic copper as well as the sulphides of this metal. Instead of the iron sulphates, the chlorides, ferrous and ferric, were formerly used with similar results, but abandoned on account of the practical difficulties with which their employment was accompanied.

Dr. Höpfner's method differs from that of Siemens, inasmuch as the chlorides of copper are employed instead of iron salts. It is also worked by a different form of apparatus. The electrolyte in the Siemens process consists of a mixture of ferrous and cupric sulphate solutions, to which is added a little free sulphuric acid to increase the conductivity. The liquor is continuously supplied to the cathode chamber, where a portion of the copper is deposited by the electric current, after which, the liquid passes down into the anode chamber and is finally drawn off at the bottom. During the downward passage the ferrous sulphate is changed into basic ferric sulphate by the action of the free sulphuric acid, which is produced by the decomposition of the cupric sulphate, which, by reason of its superior gravity, sinks to the carbon rods or plates which compose the anode. The liquor drawn off from the bottom of the anode chamber is poor in copper, and consists for the most part of neutral ferric sulphate. This solution has the property of converting the cuprous and cupric sulphides as well as the metallic copper into cupric sulphate ; thus the ferric sulphate is re-converted into ferrous sulphate, while the oxygen set free oxidises the copper.

Dr. W. Borchers, in his *Electro-Metallurgie* (1891), gives the following reactions as taking place during the process :

$$x H_2SO_4 + 2CuSO_4 + 4FeSO_4 = 2Cu + 2Fe_2(SO_4)_3 + x H_2SO_4.$$
$$x H_2SO_4 + Cu_2S + 2Fe_2(SO_4)_3 = 2CuSO_4 + 4FeSO_4 + S + x H_2SO_4.$$
$$CuO + H_2SO_4 = CuSO_4 + H_2O.$$
$$3CuO + Fe_2(SO_4)_3 = 3CuSO_4 + Fe_2O_3.$$
$$CuO + 2FeSO_4 + H_2O = CuSO_4 + Fe_2O_3 + SO_3 + H_2.$$
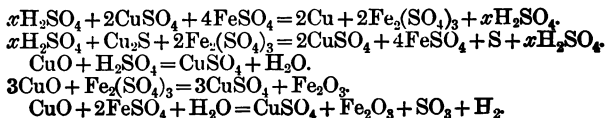
The oxidation and solution of the copper can be completely carried out with many finely pulverised sulphide ores, even in an unroasted condition, by the use of a moderately heated solution. With other ores, however, a moderate roasting of the pulp, by which the copper compounds are converted essentially into cuprous sulphide, must precede the solution of the copper. The lixiviation of the pulverised ore by means of the "decopperised" and deoxidised liquor is performed in troughs, the pulp being kept in suspension by means of mechanical stirrers. The liquor coming from the electric cells is continually fed into the head of the trough, mixed with the necessary amount of pulp, and it leaves the trough with the decopperised pulp at the other end, the solution being hastened by the application of heat, which is supplied by steam pipes in the bottom of the trough. The pulp is separated from the solution either by a settling tank or filter pump; it is now rich in copper and is deoxidised, and is therefore ready to be fed anew into the electrical apparatus. The process, as will be seen from this description, is continuous between the leaching of the ores and the electrolysis of the solution, the lixiviant being produced electrically in the decomposition cells and the electrolyte regenerated chemically by the solution of the copper in the ores. The time required for the completion of the process is about two hours, and the amount of copper remaining in the residues is stated to be from 0·1 to 0·5 per cent. whether the ore is rich or poor in metal.

ANALYSES OF ELECTROLYTIC COPPER.

S.	Cu.	Ag.	Pb.	As_2O_5.	As.	Fe.	Co and Ni.	P
—	99·824	·036	·0516	·0205	—	·0308	·006	·0014
—	99·818	·039	·0472	—	·0181	·0288	—	·0008
—	99·81	·015	trace	—	trace	·011	—	—
—	99·861	·021	·0195	—	·0201	·022	—	·001
·0042	—	·007	·008	—	·0104	·0125	—	·0004
·0028	—	·0043	trace	—	·0148	·0084	—	·001

For coating articles of brass and German silver with copper, a solution of copper sulphate is employed; but articles of zinc, iron, tin, and lead require a copper cyanide solution.

CHAPTER XX.

ZINC.

THE first reference to the metal zinc appears to have been made by the monk Albertus Magnus in the thirteenth century, but it may have been known previous to this time, as it was brought from the east by the Portuguese before it became a commercial article in Europe. It was known and sold under the name Spialter, hence the modern word Spelter. It was probably first discovered in the smelting of ores of other metals containing zinc ore and the condensation of the volatised zinc in the flues and cracks of the chimney. At any rate such deposits have been obtained in recent times from smelting a zinciferous ore in the blast furnace.

Zinc has a bluish-white colour, but its lustre is much less than that of many other metals. When cast and freshly broken it exhibits a tabular structure of brilliant cleavage planes, which, however, soon become covered with a film of oxide on exposure to the air. Its specific gravity varies from 6·8 in the cast to 7·2 in the rolled state. It is moderately soft, and at ordinary temperatures as well as at temperatures above 200° C., it is brittle. Bolley has shown that zinc is influenced by the temperature at which it has been cast. When pure, and poured into the mould just before it solidifies, its fracture is but feebly crystalline, but if the metal is made very hot and poured at a low red heat into the mould, it then becomes largely crystalline. Commercial zinc is often very impure, the chief ingredient being lead : but certain varieties are now largely sent into the market containing very small amounts of impurities. These are known as refined or double distilled spelters. Such zinc, being nearly pure, is moderately malleable at the ordinary temperature, but common zinc is only malleable at temperatures between 100° and 200° C. It is moderately ductile. Its

specific heat is ·094, and it expands $\frac{1}{340}$ of its length when heated from 0° to 100°. It melts at 415° C., and at about 1040° C. it boils, but it is volatile at a little above its melting point, and if heated in air it burns with a bluish-white flame. It contracts very little on cooling after being cast in a mould, so that it is an excellent metal for producing fine castings.

Rolled zinc has a wide application in the arts, and, whatever the application, it is advisable to re-melt it before rolling into sheets. This is generally done in a reverberatory furnace. In the case of common zinc this re-melting tends to remove impurities, which are oxidised, together with some of the zinc and form a dross. The thickness of the cast ingot is important, as it must be proportioned to the size of the finished sheet. The ingots, having been cast and raised to a temperature of 150° C., they are put through the roughing or breaking-down rolls, then cut to size, and completed in the finishing rolls. The sheets require to be carefully annealed during rolling, until the crystalline structure has been destroyed, when the metal will roll like lead without any additional annealing. Sheet zinc varies in thickness from ·002 to 1·60 inches. The making of roofing sheets is perhaps the most important and most extensive of sheet zinc manufacture. In thick plates zinc is used by engravers for zincography. Zinc dust is used as a reducing agent and in fireworks.

Chemical Properties of Zinc.—Its atomic weight is 65. Zinc is unaffected in dry air, but tarnishes in moist air with the production of a superficial film of oxide, probably in a hydrated form. It readily burns in air with a bluish-green flame, forming zinc oxide, ZnO (*lana philosophica*). The white fumes produced when casting zinc, or alloys containing zinc, are due to the formation of this oxide, which emits a characteristic odour. It is also known as flowers of zinc, zinc white, etc. It is a very stable compound and practically non-volatile. The metal zinc is not attacked by mineral lubricating oils; and of ordinary animal oils it is most affected by sperm oil, and least by lard oil. It is not poisonous. Pure zinc is insoluble in water, and almost unaffected by ordinary acids, but common zinc is soluble in boiling water, and is readily soluble in dilute hydrochloric and sulphuric acids. If, however, ordinary zinc be amalgamated, it resists the action of acids like pure zinc, hence its use in galvanic batteries to prevent local action. Pullinger states that "pure zinc with a perfectly smooth surface is not attacked by dilute sulphuric acid that has been well boiled,

but zinc with a rough surface is readily acted upon under
the same circumstances. The presence of oxidising agents
such as nitric acid, hydrogen peroxide, or electrolysed sul-
phuric acid, increases the rate of dissolution, while a reduc-
ing agent, such as hydriodic acid, almost entirely prevents
dissolution ; but reducing agents containing sulphur, such as
sulphur dioxide, are without effect. It is not improbable
that when zinc with a rough surface dissolves in dilute
sulphuric acid, the cause of dissolution is persulphuric acid,
which acts catalytically, and in all probability, pure dilute
sulphuric acid would be without action upon metallic zinc,
whether the surface of the latter be rough or smooth.

The solubility of impure zinc in dilute acids has been
generally explained on the supposition that local electric
currents are set up, owing to the presence of the impurities,
while with pure zinc no such currents are produced. Weeren,
however, shows that the insolubility of pure zinc is due simply
to the formation of a layer of condensed hydrogen on the
surface of the metal, and thus the further action of the acid
is stopped. Oxidising agents remove this film and assist
dissolution ; while in impure zinc the hydrogen, obeying
ordinary electrical laws, is evolved from the surface of the
impurities. The fact that dissolution is much promoted by
simply brushing the surface of the metal, or by allowing the
action to take place in a vacuum, appears to afford strong
support of this view, which is also quite in harmony with
the fact that pure zinc dissolves much more rapidly in boiling
dilute sulphuric acid, when the ebullition of the liquid re-
moves any hydrogen from the surface of the metal, than at
98° where no ebullition occurs. Pure zinc with a rough
surface, as Pullinger has shown, dissolves much more readily
in dilute sulphuric acid than the same metal when the
surface is perfectly smooth. Weeren suggests from the
above facts that the difference in the action of diluted sul-
phuric acid on pure and impure zinc is capable of a simple
mechanical explanation.*

Zinc and zinc oxide readily dissolve in alkalies, and zinc is
oxidised when heated with nitre or potassium chlorate. The
vapour of zinc reduces carbon dioxide at a white heat to
carbonic oxide, while at a lower temperature the oxide of zinc
is reduced by carbon or carbonic oxide. Zinc oxide is a
powerful base, uniting with acids, such as silica, to form salts,
and also with alumina to form aluminates, of which the
natural mineral, Spinel, may be taken as an example. Zinc

* Thorpe's *Dict. of Chem.*, Vol. III., p. 1048.

oxide unites with silica at very high temperatures to form silicates. $4ZnO,3SiO_2$ and $2ZnO,SiO_2$ are known. Oxide of lead combines with oxide of zinc, and forms a fusible compound.

Zinc oxide is largely prepared in America by heating the ore in a reverberatory furnace with carbon, and burning the reduced zinc by means of a blast of air. The oxide, which is carried over with the draught, is condensed in large chambers of moistened canvas. The uncondensed gases pass through this canvas, while the oxide of zinc is retained. The older European method consists in placing metallic zinc in retorts and volatilising it by heat ; the zinc, coming in contact with air in an exhaust chimney, is formed into oxide which is then carried through a long series of condensing chambers and deposited in tanks lined with cloth. The purity of colour varies with the purity of the zinc.

Zinc and sulphur do not readily combine by direct union, but if zinc filings and mercury sulphide are projected into a white hot crucible, the zinc combines with the sulphur with detonation. At lower temperatures the mercury sulphide simply volatilises. Zinc in a similar way decomposes potassium sulphide. Zinc sulphide unites with other sulphides, but these combinations are only fusible with difficulty. The following are examples : (ZnS,FeS) (ZnS,PbS) (ZnS,Sb_2S_3). When zinc sulphide is finely divided and roasted in air, a mixture of zinc oxide and zinc sulphate is formed, but at a high temperature the latter is decomposed, forming oxide. Zinc sulphide occurs in nature as the chief ore of zinc, and is roasted to oxide before reducing the metal. It is decomposed by iron and by carbon at high temperatures.

Zinc and Phosphorus.—These elements readily unite under the action of heat, and if heated in a luted glass retort a sublimate of phosphor zinc is formed, having a metallic lustre and vitreous fracture. Zinc containing phosphorus somewhat resembles lead in colour and lustre, and has a higher fusing point than pure zinc. A little phosphorus is said to increase the brilliancy of zinc, probably by removing iron as a phosphide.

Zinc and Arsenic.—Arsenic is often present in zinc in minute quantities, and the two metals readily unite when heated together, forming grey, granular, brittle alloys, which are comparatively infusible when much arsenic is present. Hydrochloric and sulphuric acids act on these alloys, evolving arseniuretted hydrogen.

ORES OF ZINC.

Zinc is practically unknown in the native state, and is found chiefly in the form of sulphide, carbonate, oxide, and silicate in somewhat limited localities. They occur in Cornwall, Derbyshire, Cumberland, and North Wales in this country ; and in Belgium, Hungary, Silesia, the Harz, and in New Jersey.

Blende, ZnS, is one of the principal sources of the metal, and is known to miners as "black Jack." It occurs crystalline and massive. When pure, as in New Jersey, it is white, but generally it is brown or almost black. It nearly always contains sulphide of iron, and very frequently galena and copper pyrites. It sometimes contains antimony and silver. Cadmium is a very frequent companion of zinc in its ores, and is extracted by the same process. The word "blende" comes from the German *blenden*, to dazzle. When pure it contains 67 per cent. of zinc, but more frequently the amount varies between 40 and 60 per cent.

Calamine, ZnCO$_3$, is a native carbonate of zinc containing 52 per cent. of the metal when pure. It is then colourless or white, with a pearly lustre, but owing to the presence of iron, manganese, etc., the colour is often brown or reddish. It breaks with a conchoidal fracture. Calamine is the most abundant ore of zinc, and is found in all the important zinc-producing districts.

Red Zinc Ore or Zincite, ZnO, is generally coloured by oxide of iron and manganese. It is white when pure. It occurs largely in New Jersey. It is often coated by a crust of zinc carbonate.

Electric Calamine, 2(2ZnO,SiO$_2$), is fairly abundant in nature, and generally associated with other zinc ores. The term "electric" is given to it because a crystal of it becomes polar when heated.

EXTRACTION OF ZINC.

Zinc, being a volatile metal, has to be separated from its ores by a process of distillation. It is necessary that the ores employed should be comparatively rich in metal, and as uniform in composition as possible. For this reason they are submitted to certain mechanical operations, such as breaking, washing, and picking, to apportion the size of the lumps and to reject the worthless matters. The ore is then calcined in

flat-bedded reverberatory furnaces, in order to remove readily volatile matter, such as water, carbon dioxide, etc., and in the case of blende, to convert it into zinc oxide. In some works a double-bedded calciner is used, in which the ore undergoes a preliminary calcination on the upper bed and is then raked down on to the lower bed, which is at a much higher temperature, to complete the action. Different kinds of furnaces and retorts have been employed for the reduction of the roasted ore, but the principle is the same in all of them. A closed vessel contains the ore mixed with carbon, and attached to it is some form of condenser for receiving and cooling the volatilised vapour. The following typical methods have been employed.

Old English Method.—Blende was largely used. It was first picked to separate the rich particles, and then reduced to small pieces by means of stamps or rolls. It was then calcined in a small reverberatory furnace in quantities of about 22 cwts. at a time. The reduction of the roasted ore was conducted in fire-clay crucibles, which were circular in transverse section and gradually widened from bottom to top. Each contained a small circular opening at the top for charging, and provided with a cover. At the bottom

Fig. 129.

was a similar but smaller opening, to which was attached an iron pipe for conducting the reduced zinc vapour to the condensing pot below. Each ordinary pot was 4 feet high, 2½ feet in diameter at the bottom, and 3½ feet at the top. The furnace employed (Fig. 129) was somewhat similar to that used at glass works, having a fire-place running along the middle, with ledges for three pots on each side. The condensing tube was made of two parts—a short iron pipe, lined with clay, attached to the pot, and another longer one passing from the first pipe to the condenser.

When charging, the hole in the bottom of the crucible was covered with wood, which was afterwards charred on heating, and prevented the solid contents from falling into the pipe. The charge for each pot was 3 cwts. of calcined blende or calamine, and 2 cwts. of coke. The lids were then luted on, and the temperature gradually raised. After a time vapours

of cadmium of a brown colour, if that metal was present, came off, and these were succeeded by bluish-white vapours of zinc and carbonic oxide. The long condensing tube was then attached. A furnace might work 5 tons of ore per fortnight and produce 2 tons of zinc. This old method involved less labour than the continental methods, but difficultly reducible ore was not decomposed. The zinc obtained was termed "rough zinc," and consisted of a non-homogeneous mass containing zinc oxide and other impurities, which were largely removed by re-melting and skimming off the dross.

Carinthian Method.—This was in principle the same as the English system. The furnace consisted of an arched chamber, heated by a wood fire, containing a number of conical clay tubes, each 40 inches long by $4\frac{1}{2}$ inches diameter at the top and $3\frac{1}{2}$ inches diameter at the bottom. The lower end was fixed into a foot-piece of clay, consisting of a short vertical tube having a flange at top. These flanges formed the bed of the reduction chamber, being supported on a trellis-work of iron bars. The bottom of each is first stopped with charcoal, the charge introduced, and the top closed. The charge consisted of calcined ore with charcoal and lime, mixed with a solution of wood ashes and salt. Each contained 5 to 6 lbs. of ore, leaving a space of 4 inches at top which was filled with charcoal. The charge was worked off in thirty to forty hours, and the furnace cooled before the addition of a fresh charge. This entailed great loss, and finally resulted in its abandonment.
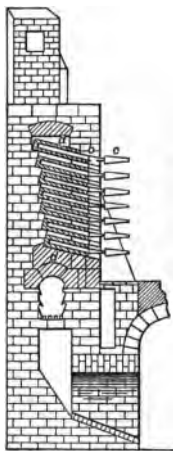
Fig. 130.

Belgian Method.—This process was first practised at Liège, in 1810, where the large deposits of calamine existing in the district were smelted. The furnaces employed at Vieille Montagne, said to be the largest zinc smelting establishment in the world, are arranged in series of four, and of the general form represented in Fig. 130. Each furnace contains a vertical arched chamber in which are placed several rows of cylindrical fire-clay retorts a, arranged in parallel rows, one above the other. Below this chamber is the fire-place. In the front part of the chamber is a series of cast-iron shelves, inclining slightly downwards,

and on these are placed fire-clay slabs. At the back of the chamber is a series of ledges on which the closed ends of the retorts rest. The whole is divided into rectangular compartments, each containing two retorts. This inclination of the retorts causes any corrosive slag to flow down to the coolest part, where it is less injurious. Each retort is fitted with a simple bellied fire-clay nozzle in which the distilled zinc for the most part condenses,.and to the front of this is attached a sheet-iron conical tube to condense the fume, which is a mixture of zinc and zinc oxide. In some works a simple clay condenser has been used. The retorts are 39 to 42 inches long, and 6 to 8 inches internal diameter.

The charge of roasted ore and coal varies in the different retorts according to their position in the furnace, since the lower ones are more highly heated than the upper ones, and therefore can carry a greater charge. This consists of 28 lbs., and 16 lbs. in the upper ones. Moreover, the less refractory materials, such as zinc fume and ores, with much oxide of iron, are placed in the upper row of retorts in consequence of their lower temperature. The retorts in the lowest row are generally left empty, so as to protect the next row from the intense heat. The number of retorts in a furnace varies from sixty to eighty. When starting a new furnace the temperature is gradually raised to a white heat, the charges are then introduced, and when a greenish-white flame is seen the iron pipes are luted on with fire-clay and the operation continued until the reduction is complete. About 1 ton of ore is treated in this furnace in twenty-four hours, producing about 950 lbs. of zinc ; but this varies with the richness of the ore. Each condenser contains 1 to 2 lbs. of zinc, which is ladled or raked out every two hours. The crude zinc thus obtained requires to be re-melted, when zinc oxide and other impurities largely rise to the surface as dross. The metal is then cast into ingots, weighing 70 to 80 lbs. By the invention of M. Dor the Belgian retorts are subjected to a pressure of 3000 lbs. per square inch during manufacture. They are afterwards bored by machinery, so as to get them thin and yet very durable.

Silesian Method.—This method, which is now modified, was formerly carried out as follows : The furnace employed is shown in Fig. 131, and consists of a chamber containing a series of muffle-shaped retorts made of fire-clay, a row of retorts being placed on each side of the central fire-place. In the upper part of the mouth of each muffle is fixed an elbow-shaped clay nozzle, which is connected at the other

end with an iron pipe leading into a small chamber where the distilled zinc condenses. The muffles are 3 feet long, 18 inches high, and 8 inches wide. The bed of the chamber on which the muffles rest is flat, and bounded on each side by six equal arched recesses, each of which contains two retorts, arranged back to back. The fire-place does not pass right through the furnace, but is stopped at some distance from the back ; and the flame, after circulating round the muffles, is drawn downwards into a lower flue, so as to heat the bottom of the muffles. 70 lbs. of the previously calcined calamine is mixed with 32 lbs. of coke and coal dust, and charged into the hot muffles, when the temperature is gradually raised to the proper degree. At first only moisture is expelled, but after a few hours the greenish-white flame of zinc is seen, when the condensing pipes are attached and the operation continued till the oxide of zinc is reduced. In a more recent form of Silesian furnace, the muffles are placed in two rows, one above the other, each row containing sixteen muffles. The muffles are also made much larger than formerly, and the capacity of each furnace has been enlarged to take a charge of 6 to 8 tons.
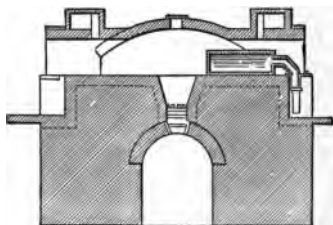
Fig. 181.

In the zinc works of Prince Hohenlohe, in Silesia, there are a total of 106 furnaces, and a separate roasting works for the preparation of zinc blende for reduction. The roasting is performed in long double-bedded reverberatory furnaces, each having an output of 220 cwts. every five hours. Each reduction chamber contains thirty-two muffles heated by gas from Boetius producers. Calamine is used in the raw state, and the charge for each muffle is 507 lbs. The zinc obtained is very impure, often containing 3 to 4 per cent. of lead. The refining of the crude zinc is conducted in a reverberatory furnace, with an inclined bed having a depression or well in which the metal collects, the lead at the bottom and the zinc on the top. By this means the amount of lead is reduced to 1 per cent., the iron to ·02 per cent., and the sulphur to ·04 per cent. At Freiberg the Silesian furnaces are heated with gas, having regenerative chambers underneath the retort

chambers, and arranged on the well-known Siemens system. Each muffle receives 100 lbs. of calcined ore, which requires twenty-four hours for distillation, and yields about 32 lbs. of zinc. The old method of condensation in chambers has now largely given place to the Belgian system of external nozzles and iron pipes. The introduction of gas firing has resulted in a considerable saving of fuel, which was formerly $3\frac{1}{2}$ tons of coal per ton of ore, and is now reduced to less than half
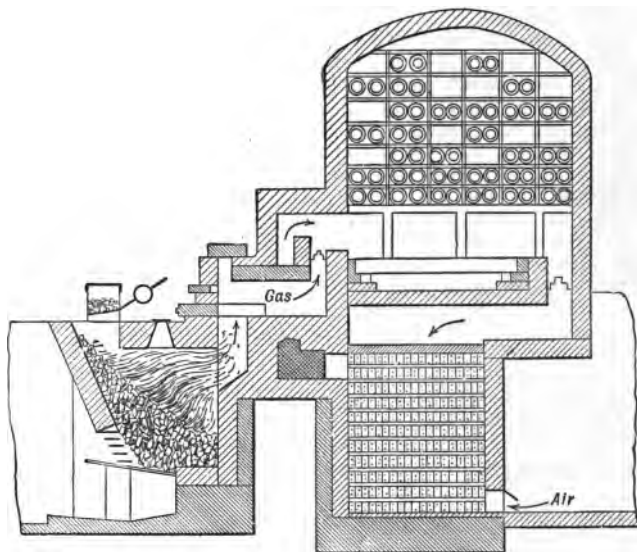
Fig. 132.

that amount. A proposed method of heating a Belgian zinc furnace is shown in Fig. 132. The gas passes direct to the combustion chamber, but the air is heated by a recuperator which contains alternate channels in refractory brickwork, so that the waste gas passes downwards through one set, while the air for combustion is heated by passing upwards through the other set. The retort chamber is shown with a number of clay retorts in section, and certain spaces are left vacant for the reception of other retorts.

Blast Furnace.—Many attempts have been made to reduce zinc ores in the blast furnace, but without much success. This is owing to the fact that the furnace gases and zinc vapours must pass away together, and during the condensation which ensues, the zinc and carbon dioxide react on each other, with the oxidation of the zinc and the formation of carbonic oxide. Lencauchez found that this oxidation of zinc still occurred when the proportion of carbon dioxide was only ·5 per cent. of the gas employed. By very rapid cooling he reduced the oxidation of the zinc to as little as 5 per cent., but concluded that this method of extraction was not commercially practicable.

In 1878 Binon & Grandfils introduced the method of treating zinc ores in vertical retorts on the old Carinthian principle, but using gas as a source of heat. Harmet used a shaft furnace, and led the zinc vapours through two upright cylinders filled with incandescent fuel, so as to reduce carbon dioxide to carbonic oxide. Quagleo & Lentz in 1884 patented a method which consists of reducing carbon dioxide to carbonic oxide in such a way that the apparatus at the same time forms a carbonic oxide generator in which the heat produced by the combustion of carbon to carbonic oxide is utilised, and the carbonic oxide employed as a reducing gas. The furnace arrangement consisted of two shafts containing ore and fuel, connected by a canal, into one of which air was introduced, and from the other the products of reaction were withdrawn ; this constantly being reversed. Steger has suggested that if enough heat is generated for the reduction of the zinc oxide and zinc vapours, led into a cool receptacle in which is an atmosphere of carbonic oxide, then the zinc will be condensed and not oxidised. The atmosphere of carbonic oxide may be produced by the use of a hot blast at a temperature of 1200° C., when only a trace of carbon dioxide will be produced. Steger recommended horizontal ovens in which zinc ore and coal were placed, and when the furnace was brought to bright red heat by a very hot blast, reduction ensued. Walsh proposed to reduce zinc oxide in a blast furnace with a closed top, and to pass the gases and vapours over strongly heated carbon in a chamber connected with the reduction furnace. The vapours were then passed through a condenser, consisting of two parallel and horizontal iron pipes connected together by a series of U shaped tubes. The apparatus was maintained at such a temperature that the condensed zinc remained in the liquid condition.

Wet Methods.—No successful wet or electro-chemical methods have been yet devised for the extraction of zinc, although many attempts have been made. The following are some of the most noteworthy:

Parnell employed a process for the treatment of complex ores containing zinc, in which the ore was first roasted to oxide, then dissolved in dilute sulphuric acid, which was obtained as a by-product, the copper was precipitated by iron, and the residual liquor evaporated to dryness. This was strongly heated with zinc sulphide, when the crude oxide so obtained was sold to zinc smelters.

Maxwell Lyte proposed to roast the ore to oxide, and to dissolve it in hot hydrochloric acid. The lead was allowed to crystallise out as chloride, and the iron was precipitated by

A. Tank for Solvent.
B. Lixiviation Vats
C. Reservoir for Solution.
D. Feeding Pipe.
E. Electro Depositing Vats.
F. Cistern for Spent Solution.
G. Pump.
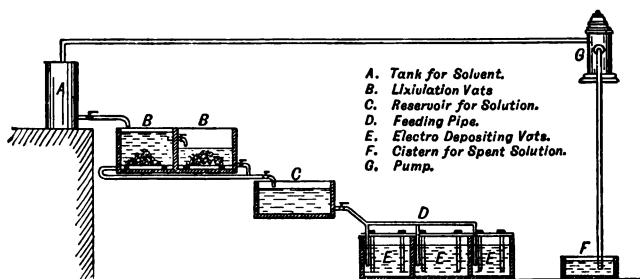
Fig. 133.

limestone. The copper was precipitated with scrap iron, and the zinc afterwards precipitated as oxide by lime.

Létrange (Fig. 133) introduced an electrolytic method for zinc. Blende was roasted at a comparatively low temperature so as to form sulphate of zinc, which was dissolved in very dilute sulphuric acid. The solution was then electrolysed with lead or carbon as an anode, and zinc as a cathode.

Kiliani of Munich also patented a method of extracting zinc by electrolysis. The oxidised ore was placed in lead-lined wooden vats, and digested with a solution of ammonia and ammonium carbonate until the solution was saturated with zinc. The liquid was then filtered and placed in tanks, where it was fed into the depositing tanks. The cathodes were of zinc or brass and the anodes of sheet iron. A part of the zinc was deposited on to the cathodes and oxygen given

off at the anodes. The liquid passed through the vats at a speed which was regulated according to the amount of zinc present and the strength of the current. The vats were covered to prevent loss of ammonia.

ZINC FUME.

This is produced in the form of a grey dust, and collects in the sheet-iron pipes at the end of the condensers in the Belgian furnace, and in the other forms of condensers. It consists largely of zinc, but contains also zinc oxide and small quantities of foreign metals, such as lead, cadmium, arsenic, etc. An analysis in Percy's *Metallurgy* is as follows:

Zinc,	.	.	.	.	.	97·82
Iron,	.	.	.	.	.	·16
Lead,	.	.	.	.	.	·23
Cadmium and arsenic,		.	.	·08

The amount of oxygen is not stated. This fume is readily oxidised, producing considerable heat, hence it is a powerful reducing agent. It is generally added to fresh ore, and distilled in the retorts. A method formerly much used for the treatment of zinc fume was conducted in the *Montefiori* furnace. It depends on the principle that when fume is heated to the melting point of zinc without the accession of air, and at the same time subjected to pressure, the finely divided particles of zinc coalesce and form a liquid mass, leaving zinc oxide to the amount of about 8 to 10 per cent.

The pot in which the fume is heated is a hollow cylinder, closed at the bottom and open at the top, 27 inches deep and 7 to 8 inches in diameter. At the bottom is fixed a tube at right angles, the bore widening towards the junction of the vessel. Both are made of clay. These pots or tubes are placed vertically in the chamber on two sides of a vertical wall, and heated by a fire beneath the level of the platform which supports the cylinders, while the flame and products of combustion pass into the chamber through holes in the arched roof of the fire-place. The bell-mouthed pipes fixed at right angles to the pot open beyond the outer walls of the chamber, each being fitted with a clay plug. The top of each pot is provided with a clay piston connected with an iron rod. These rods project beyond the flat roof, having suitable handles with four radial arms, so that pressure

may be applied without admitting air, and the liquid zinc is extracted by means of the lateral tube. Such metal, however, requires re-melting to purify it.

Effects of Various Metals on Zinc.—Iron is generally present in zinc, but only in very minute quantities. $1\frac{1}{2}$ per cent. of iron renders zinc unfit for rolling, and a much less quantity is hurtful when lead is also present, which, in common zinc, is about 1 per cent. Iron causes the zinc to heat so much in rolling as to require frequent cooling to prevent cracking. This is not the case with pure zinc. Karsten states that ·2 per cent. of iron in zinc for rolling is the maximum amount that is permissible. Iron may be removed from zinc by re-distilling. Cadmium somewhat increases the hardness and brittleness of zinc, but not so much as the other impurities likely to be present. Lead is always present, although in the double refined spelters its amount is very small. Zinc is capable of uniting with 1·2 per cent. of lead, and lead can dissolve 1·6 per cent. of zinc. Any amount over these proportions will largely separate out on cooling. Silver combines with zinc, and when zinc is melted with argentiferous lead, the zinc separates out at a certain point in the cooling of the mixed metals, carrying the silver with it and some of the lead. This is the principle of the Parkes process for desilverising lead. The refining of zinc, in order to remove its impurities, has been already explained. For the alloys of zinc, see the Chapter on Alloys.

CHAPTER XXI.

TIN (Stannum).

Tin was one of the first metals known to mankind, owing to its occurrence in nature in the state of an easily reducible oxide. It is mentioned as well known in the time of Moses, and the Phoenicians obtained it from Cornwall and the Scilly islands long before the Christian era. The British islands were called Cassiterides. The term *stannum* for tin was applied in the fourth century. Pliny confounded tin and lead together, calling the one *plumbum album* and the other *plumbum nigrum*.

Tin is one of the whitest of metals, but has a faint yellow tinge, and when warmed emits a slight characteristic odour. It is one of the least tenacious of the useful metals, having a tensile strength of 6 tons per square inch. It is, however, extremely malleable, and can be reduced to very thin leaves, termed *tinfoil*. When a bar of tin is bent it gives a peculiar crackling noise, known as the "cry," which is generally attributed to the crystals grinding over each other. Tin is exceedingly prone to crystallise, as is shown when the surface is washed with dilute aqua regia. This effect is known as *moirée metallique*, and due to the unequal reflection of light by the facets of the crystals. Its specific gravity is 7·29, and this is scarcely increased by rolling. It melts at 227° C., and is not readily volatile. When it is just melted and allowed to cool, the surface remains bright if the metal is pure ; but the presence of a little lead, iron, etc., tends to impart a duller lustre, and, if in quantity, a frosted appearance. The impurities in common tin are : lead, iron, arsenic, copper, bismuth, tungsten, and sometimes manganese and zinc. The best kinds of commercial tin are remarkably pure, as in a number of analyses made by the author only a faint trace of iron could be obtained, and no indication of other metals

was observed. The presence of a little copper is advantageous in tin employed for tinning iron. The specific heat of tin is ·056, its co-efficient of linear expansion is ·000022. It is a poor conductor of heat and electricity, being about one-seventh that of silver. It is capable of assuming allotropic forms, since ordinary tin crumbles to a grey needle-like powder when exposed to a very low temperature.

Tin does not oxidise at ordinary temperatures, even in moist air, hence its great value as a coating for other metals which readily corrode ; but if it is heated much above its melting point it oxidises, forming the white oxide SnO_2. At a strong white heat it burns with a bright flame, forming the dioxide which is the chief and most stable oxide of tin. It is used for imparting whiteness to enamels, in grinding glass, and in polishing steel, etc. An impure form is thus largely used under the name of "putty powder." It is precipitated in the hydrated form when tin is oxidised by nitric acid. Heated with hydrogen, carbonic oxide, carbon, and potassium cyanide, it is reduced to the metallic state. Tin is insoluble in nitric acid, but dissolves in aqueous or fused alkalies with the formation of stannates. It is also soluble in either strong sulphuric or hydrochloric acid. By fusion with sulphur it forms sulphide of tin, and by ignition in chlorine gas it is converted into stannic chloride.

Tin and sulphur combine when heated together, forming a tough, crystalline, bluish-grey, fusible mass, which is converted into stannic oxide by roasting in air, and partially reduced by fusing with iron.

Tin and phosphorus readily combine to form highly crystalline compounds, known as phosphor tin. A similar compound with arsenic may be obtained by heating tin and arsenic together.

Ores of Tin.—Cassiterite, SnO_2, is the most important ore of tin. It occurs in combination with ores of lead, copper, and zinc, mixed with a gangue of granite, fluor-spar, porphyry, etc., in Cornwall and Devon. The largest quantities are obtained from the above counties and from Banca (Straits tin). Small quantities occur in Germany, Austria, New South Wales, Bolivia, United States, Spain, Siberia, and Russia. Tin-stone crystallises in the tetragonal system, but is also found massive and in grains. Tin pyrites, SnS_2, also occasionally occurs in Cornwall and Bohemia. It is opaque, with a steel-grey colour and black streak. By the disintegration of rocks containing tin ore, the mineral is washed out and carried forward by running water. This has given

rise to a number of alluvial deposits known as stream tin. This variety is noted for its purity, but is almost worked out in this country.

METHODS OF EXTRACTION.

The ores in vein tin, as already mentioned, are frequently associated with ores of other metals, as well as with various kinds of gangue. This necessitates mechanical preparations previous to the smelting operations, so as to separate foreign ingredients as far as possible from the tin ore. After a preliminary washing the materials are sorted and divided into various classes, of which the following may be taken as types :

I. Ores which are rich in tin. II. Ores of tin mixed with ores of other metals. III. Ores of tin and copper. IV. Useless materials containing little or no useful metal.

Ores of Class I. are crushed by stamps or rolls to a certain degree of fineness and sized by means of sieves. The method of stamping tin ore is very similar to that described for silver ores, and therefore the description of a stamp battery need not be repeated here. A supply of water is fed into the mortars, and the material passes out in the form of a mud; this is concentrated by means of buddles or other washing apparatus, which effects the separation of the tin oxide in virtue of its high specific gravity, and this washing can be profitably used when thè ore contains less than 1 per cent. of tin. In the washing apparatus the mud is subjected to a slow revolving or shaking motion, by which the denser portions collect in one direction while the lighter portions are washed away by the stream of water. The latter are conducted into settling tanks, where the finer portions of the ore which have been carried away by the stream may be deposited and worked over again in another operation. In all cases the ore should be crushed to such a degree of fineness as to cause the fragments to be of fairly uniform size. If the crushing is too fine, much of the ore is very liable to be lost in the washings. The sands from some ores after washing have a white metallic appearance from the presence of arsenical and iron pyrites, when they require to be calcined before they are submitted to reduction.

The calciners are of the usual reverberatory type, some of them having special features. The ordinary reverberatory furnace is 12 to 15 feet long, 7 to 9 feet wide in the middle, with a low arch about 2 feet above the bed and sinking

gradually towards the flue. The ore is charged through a hopper from the top, and raked out through a door at the flue end when roasted. About 15 to 20 cwts. of the crushed and dried ore are charged in at one time. The temperature is gradually raised, and the mass is frequently rabbled to bring all portions in contact with the air which is passing over it. If the heat is raised too rapidly, a fusible sulphide and arsenide
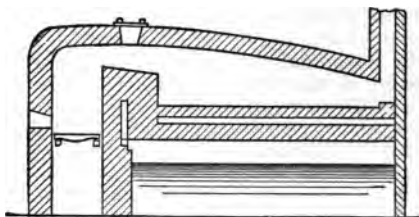
Fig. 134.
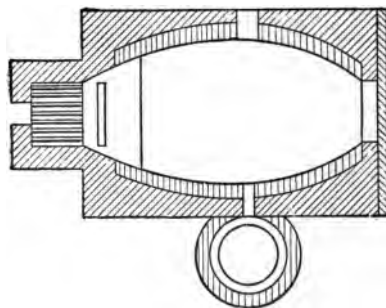
Fig. 134A.

of tin is formed, causing the mass to clot together and necessitating a re-grinding before proceeding with the cal-cination. After withdrawing the charge from the furnace, it is exposed in small heaps to the action of the atmosphere to promote the oxidation of any remaining sulphides into sulphates. The ore is next washed in vats with water to dissolve out the soluble sulphates of iron, copper, etc. The

residue is washed again on a rack table to remove the lighter
and earthy portions. The heavier portion is then termed
black tin, and after drying is ready for smelting.

The smelting furnace is a reverberatory, about 18 feet × 9
feet, having a low slanting roof (Fig. 134). The fire-bridge
is hollow, and the bed slants from all parts towards the
tap hole, beneath which is an iron basin, lined with clay,
to receive the molten tin. The bed is formed of iron,
covered with slate and lined internally with 7 to 8 inches
of fire-clay, and resting on this are fire-bricks set edgeways.
20 to 30 cwts. of ore are mixed with one fifth their weight
of anthracite and spread uniformly over the furnace bottom,
and if the ore is refractory a little fluor-spar or lime is
added. The side doors are then luted up and the tap hole
stopped with clay. The temperature is
gradually raised for five or six hours,
when the door is opened and the charge
rabbled. More anthracite is thrown on,
the mass heated for another forty-five
minutes and again rabbled, when the
metal is ready for tapping. Part of the
slag is thick and is raked out of the
furnace, while the fluid slag is run out
with the metal. The slag is chiefly a
silicate of iron, but often contains suffi-
cient tin to enable it to be smelted with
a fresh charge. For the above quantity
of ore 15 cwts. of coal are required as
fuel, and 5 cwts. of anthracite for re-
duction of the metal.
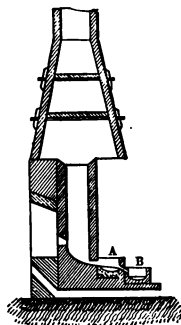
Fig. 135.

In Germany, tin ore is smelted in a
small charcoal blast furnace (Fig. 135).
It is built of granite and covered with a hood at the
top. The metal and slag flow into the receptacle A, and
the liquid slag on the surface flows along a gutter into a
vessel B, containing water, in order to make it brittle, so
that it may be easily broken up for re-smelting to recover
the tin it contains. The tin obtained from the blast furnace
is said to be purer than that from the reverberatory method,
but there is a greater loss in the slag. The tin, as it is
reduced, flows into the first basin, then overflows into the
second, where it is left for some time to settle. The tin separ-
ates in layers according to the purity, the top portions being
the most pure and the bottom the most impure, which is
again re-smelted.

Refining.—The impure tin obtained by the above smelting processes requires to be submitted to a refining operation. This generally consists of two parts, (1) liquation, (2) poling. The refining is conducted in a similar furnace to that of Fig. 134, and about 18 to 20 tons are operated upon at one time. The temperature is raised to a little higher than the melting point of tin, and the metal then liquates out and flows into a kettle capable of holding several tons. An impure and unmelted mass containing about 20 per cent. of tin is left in the furnace, termed "hard head." It contains the impurities, such as copper, iron, arsenic, sulphur, etc., and is a hard, white, brittle, metallic mass. It is calcined and smelted with a fresh charge for the recovery of the tin. The metal which has been collected in the kettle is then melted, and submitted to the operation of poling, which consists of plunging a pole of green wood into the metal. This causes a violent agitation, due to the escape of gases, and brings the impurities to the surface in the form of dross. The same effect is produced by raising portions of the tin in a ladle and allowing it to fall from a height back again into the kettle, termed "tossing," by which means the impurities are oxidised and a dross is formed as before.

For "common" tin the metal is ladled from the refining pot into moulds. For "refined" tin purer ores are employed for its extraction, and the poling operation continued longer. The metal is then allowed to settle. The upper portion, being the purest, is preserved for "grain" tin, the middle portion for common tin, and the bottom layers require to undergo another liquation and poling. The moulds used for casting are made of granite, and the ingots are known as "block" tin.

The peculiar columnar structure of grain tin is produced by dropping the metal from a height or breaking it with a hammer when on the point of melting.

Tin is very largely employed as a coating on sheets of iron known as tin-plates. At the present time the iron formerly made in fineries has been largely replaced by mild steel, chiefly that made by the Siemens process. Tin is an important constituent of many alloys, such as bronze, pewter, Britannia metal, soft solder, type metal, bearing metals, fusible alloys, etc. It was formerly much used in the form of foil which was amalgamated with mercury for "silvering" mirrors. It has an important application in the form of pipes for distilling purposes. Culinary vessels are also coated with tin to resist the action of the atmosphere and

of vegetable acids.   Wire and other forms into which metals
are made are also often coated with tin, such as pins, for
example.   The process of boiling white, as it is termed,
consists of boiling brass articles with a solution of cream of
tartar, alum, and common salt, containing granulated tin ;
the latter is oxidised and then deposited in the metallic
state upon the brass, due to voltaic action.   Copper utensils
are tinned by first thoroughly cleaning, then heating and
rubbing the surface with sal-ammoniac (NH_4Cl) to remove
any oxide, and well rubbing in the molten tin with a piece
of tow.   The use of tin in the form of tinfoil has been
already alluded to.

Pure tin may be obtained by oxidising commercial tin with
nitric acid and reducing the oxide with potassium cyanide.
Or by electrolysing a solution of pure stannous chloride, using
platinum electrodes.

Oxland's Process.—This method was introduced by
Mr. Oxland, and was formerly much used for separating
wolfram, a tungstate of iron and manganese, from tin oxide.
The ore is fused with carbonate or sulphate of soda in a
special kind of reverberatory furnace, the hearth being
formed of an iron pan.   The flame passes over the top, and
is then drawn back under the bottom before passing to the
chimney.   The use of an iron base prevents the formation of
silicates of tin.   About half a ton of ore is treated in six
hours, the mass being frequently rabbled.   The roasted mass
is then withdrawn from the furnace, allowed to cool, and
broken up into small lumps.   The ore is then washed in a
cistern of water to remove the soluble tungstate of soda, and
the oxide of tin smelted as usual.

CHAPTER XXII.

NICKEL AND COBALT.

Nickel was discovered by Cronstedt in 1751, who obtained it from kupfer-nickel, or false copper, Ni_2As. Nickel is a brilliant white metal with a steel-grey tinge, which is especially observable when it is compared with silver. It is malleable and ductile when refined. It is a weldable metal, and when rolled into thin sheets can be welded on to iron or steel. Its melting point is below that of iron, being 1420° C. according to Le Chatelier. Roberts-Austen gives it as 1600° C., which is probably too high. It is magnetic at ordinary temperatures, but at 250° it temporarily loses this property. It is one of the hardest of metals, and is in consequence used as a protective coating for some other metals. Its specific gravity is 8·8, and its atomic weight 58·6. It readily unites with oxygen when heated, forming the oxide NiO. It is not readily oxidisable at ordinary temperatures, and resists the action of salt water better than do most base metals. It readily unites with sulphur to form the sulphide NiS, which is brass-yellow in colour; and also with arsenic to form nickel arsenide, Ni_2As. It rapidly dissolves in nitric acid, and slowly in dilute sulphuric and hydrochloric acids. Acetic and some other organic acids have little action on it unless they are acting for a long time. Caustic alkalies have no action on it, and nickel crucibles may therefore be used for fusion of substances with potash and soda. Nickel readily takes up carbon and silicon when fused in contact with carbon and silica, being thus rendered harder and brittle. Boussingault exposed pure nickel at a high temperature to a cementation process with carbon for several days, and found the metal had combined with ·37 per cent. of carbon. On submitting this to a fresh cementation, the carbon increased to ·6. On fusing this metal in a crucible

lined with carbon, a button was obtained containing ·8 per cent. of combined carbon and 1·6 per cent. of graphite. The carbon taken up in the last operation was almost all graphite. Notwithstanding this content of carbon, which makes the metal harder, it does not give the nickel the properties of hardening and tempering like steel.

Ores.—These are found in Saxony, Norway, Sweden, Spain, Russia, and Canada, chiefly in the forms of kupfernickel Ni_2As, nickel pyrites NiS, nickel glance $Ni(AsS)_2$. These ores are seldom pure, frequently being associated with cobalt, antimony, copper, iron, etc. Nickel is always present in meteoric iron. In New Caledonia, South Pacific Ocean, a hydrated silicate of nickel and magnesium was discovered about 30 years ago, and termed Garnierite, after the name of its discoverer. It has a green colour, and its formula has been given as $2(NiMg)_6Si_4O_{13}+3H_2O$, and it was at first mistaken for copper ore. Besides garnierite, there occurs in the same locality a manganiferous ore containing nickel and cobalt. The following table gives typical samples of nickel ores :

	Garnierite.	Arsenical Ore.
Nickel oxide, ...	12·00	7·64
Iron, ...	7·08	16·90
Alumina, ...	1·54	—
Lime, ...	·80	6·34
Magnesia, ...	22·05	6·35
Silica, ...	40·23	8·52
Water, ...	16·30	1·03
Sulphur, ...	—	18·73
Copper and antimony, . .	—	15·89
Carbon dioxide, . . .	—	5·68
Arsenic, ...	—	12·71

Methods of Extraction.—The treatment of arsenical and cuprous ores consists of three stages : (1) concentration by roasting to form regulus or speise ; (2) conversion of regulus or speise into oxide by dry or wet methods ; (3) reduction of nickel oxide by carbon. The following principles are involved in the above treatment, assuming cobalt to be present :

1. When sulphides or arsenides of nickel and cobalt are fused with an acid silicate of iron, the cobalt passes largely

into the slag, but the nickel does not leave the regulus or speise.

2. When oxides of nickel or cobalt are smelted with sulphur or arsenic, the nickel unites with the sulphur or arsenic, but the cobalt only partially.

3. When silicates of nickel and cobalt are fused with sulphur or arsenic, the nickel forms a regulus or speise, but the cobalt chiefly remains as a silicate.

The wet method of extraction is represented in the scheme on following page (Fig. 136).

The ore is first submitted to a preliminary roasting to remove excess of sulphur, arsenic, and other volatile matters: ferric oxide being but little soluble, the remaining portion is dissolved in hot hydrochloric acid. Bleaching powder is added to peroxidise any iron, which is precipitated as oxide and basic arseniate of iron; but if the temperature should exceed 40° C. some nickel and cobalt are also precipitated. The filtrate is treated with sulphuretted hydrogen, which precipitates copper as sulphide. The filtrate containing nickel and cobalt is boiled to expel sulphuretted hydrogen and neutralised with lime. Oxide of cobalt is precipitated with bleaching powder and the solution filtered. Hydrated oxide of nickel is precipitated by boiling with milk of lime. Nickel oxide is reduced by carbon.

Oxide of nickel is generally reduced without melting by making it into a paste with carbon, cutting the paste into cakes or cubes, placing these in crucibles or tubes, and raising them to a white heat while surrounded with charcoal.

Treatment of New Caledonian Ores.—The ores were formerly smelted near the mines, so as to concentrate the material before exporting to Europe. This was done by smelting in a blast furnace, using lime as a flux. The product was a crude alloy of nickel and iron, containing carbon, iron, and sulphur. This crude alloy was refined by smelting in a blast furnace with gypsum ($CaSO_4$), which yields sulphur to the nickel. The preliminary smelting is now abandoned, the raw ore being smelted with gypsum direct. The ore is mixed with 50 per cent. gypsum and 5 per cent. lime, compressed into blocks with water, and then dried ready for smelting. A low water-jacketed cupola, 10 feet high by 6 feet wide, is used, and works continuously, producing a regulus of nickel and iron and a slag which is a silicate of lime, magnesia and alumina containing iron. The method of refining the regulus so as to remove the impurities is based on the superior affinity of nickel for sulphur and iron

for oxygen. When the regulus has been ground to a powder, it is roasted in a long reverberatory furnace for
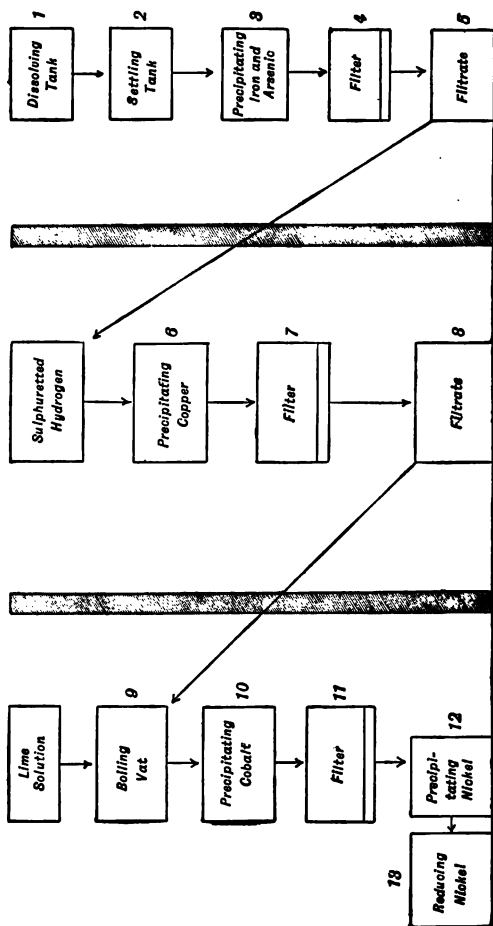
Fig. 184.

a time, depending on the amount of iron to be oxidised; then mixed with sand and transferred to another reverberatory furnace, in which the roasted regulus is melted. The oxide of iron unites with the silica to form a fusible silicate or slag, and the nickel remains in combination with sulphur. The slag is tapped out into sand moulds at the front, and the regulus removed through a separate opening at the side. These operations are repeated until the iron is removed, but the slags become more and more nickeliferous as the amount of iron to be removed becomes smaller. They are re-smelted with gypsum and sand in a cupola, when a further regulus or matt of nickel and iron is obtained. When these poor matts are sufficiently concentrated, they are treated in the reverberatory furnace along with the richer ones from the ore. The rich sulphide of nickel, after the removal of the iron, is placed on the bed of a small reverberatory furnace, and roasted until the sulphur is removed and the nickel converted entirely into oxide, which is then reduced in the usual way by charcoal.

Instead of the above reverberatory treatment the regulus may be blown in a Bessemer converter, with a blast pressure of 15 inches of mercury. The combustion of the sulphur causes the temperature of the bath to rise, and sand is added to slag off the oxide of iron. When the slag shows the presence of nickel it is run off, and the concentrated regulus poured. It will probably contain less than ·5 per cent. of iron. Any cobalt originally present will remain in the regulus. The slag is generally much richer in nickel than that produced in the reverberatory furnace. Nickel having a very high melting point, it is not possible to continue the blow until the whole of the sulphur is removed. If copper is present it will be found in the regulus. The regulus is next crushed and roasted in a reverberatory furnace, and requires about six hours if copper is present, but if copper is absent the operation will require eight hours. The requisite temperature for roasting is a dull red heat and a bright red heat for finishing. The product should not contain more than 1 per cent. of sulphur, and is chiefly in the form of oxide. It is moulded into small pieces with flour, dried, and reduced in a kind of Belgian zinc retort open at both ends, and heated in a reverberatory furnace. Such a furnace, holding twenty-two retorts, will serve for the reduction of $1\frac{1}{2}$ tons of nickel oxide with the consumption of 2 tons of coal.

Nickel, as obtained from the reduction of its oxide by

carbon, has a dull grey colour, somewhat crystalline and brittle. Ordinary commercial nickel is not pure, but it may be purified and rendered more tough and malleable by the method of Dr. Fleitman, which consists of melting the nickel in a crucible, and adding about ·1 per cent. of magnesium, which is then well stirred into the nickel. It is supposed to act as a deoxidiser. Manganese, phosphorus, and aluminium have also been used for the same purpose.

Instead of concentrating nickel with sulphur, as described in the above method, arsenic performs a similar function in arsenical ores of nickel. Nickel speise is a white, brittle, metallic-looking body consisting of nickel, arsenic, sulphur, antimony, iron, and other impurities that may be present in the ore. The composition is somewhat varied, as shown by the following analyses :

<div align="center">NICKEL SPEISE.</div>

Nickel,	.	.	.	.	.	55·9	51·6
Cobalt,	.	.	.	.	.	2·3	3·2
Arsenic,	.	.	.	.	.	30·4	34·3
Iron, .	.	.	.	.	.	1·2	2·1
Copper,	.	.	.	.	.	1·5	1·6
Sulphur,	.	.	.	.	.	8·7	7·2
						100	100

When pure dry carbon monoxide is passed over finely divided nickel at 30° C., a peculiar volatile liquid, having the composition $Ni(CO)_4$ and termed nickel carbonyl, or nickel carbon monoxide, is obtained. It solidifies at −25° C., boils at 43° C., and has a specific gravity of 1·32 at 17° C. Its vapour, on heating to 60° C., explodes violently, and if passed through a heated tube mixed with other gases, it deposits a mirror of pure nickel. Iron seems to form a similar compound, which has not, however, been prepared in a pure condition. It has been proposed to prepare pure nickel in this way. Two compounds of carbon monoxide with iron have also recently been obtained—one liquid, having the composition $Fe(CO)_5$, and the other solid, having the formula $Fe_2(CO)_7$.[*]

Nickel Plating.—Double sulphate of nickel and ammonia is dissolved in water, and the solution tested with blue litmus paper ; if acid, ammonia must be cautiously added

until the solution is slightly alkaline. The above double salt may be made by the battery method, thus :

Suspend a large plate of nickel in sulphuric acid, and connect it with the carbon pole of the battery. Place a small plate in connection with the zinc. Pass the current until sufficient nickel has been dissolved from the anode, which is determined by weighing it before and after the ex-· periment. The solution is then neutralised with ammonia. To each ounce of nickel sulphate in solution, add 1 ounce of ammonium sulphate, and test with litmus paper as described above. All articles to be nickel plated, must be clean and polished very bright. A dry process of preparing work for receiving a deposit of nickel is in successful operation. After the work has been well polished, it is thoroughly rubbed over with dry whitening, which is rubbed off, and the article suspended in the nickeling solution. A strong current is used at first so that the work may be struck as quickly as possible.

As nickel solutions are used in the concentrated state, the nickel salt begins to crystallise after a time, especially in a warm place ; in which case water must be added. It should also be borne in mind that the anode does not maintain the strength of the solution, so that it is necessary to add crystals of the double salt from time to time to replenish the weakened solution.

COBALT (Co).

Cobalt is a metal of a steel-grey colour, with a reddish cast, and very similar to nickel in many of its properties. Its specific gravity is 8·5 ; it is extremely malleable and very tenacious. Deville states that its tenacity is double that of iron. It does not oxidise at ordinary temperatures, but at a red heat forms a mixture of CoO and Co_3O_4. Cobalt forms with tin a somewhat ductile alloy of a violet colour; with iron, a hard alloy ; and with brass it forms alloys resembling German silver. Cobalt has comparatively little application in the metallic state, and may be prepared, like nickel, by first converting it into oxide and then reducing with carbon. Pure cobalt is prepared by strongly igniting cobalt oxalate $Co(CO_2)_2$, when CO_2 is evolved and the metal left as a powder. A button of metal may be obtained by fusion in a lime crucible. It may also be obtained as a grey powder by igniting the oxide at a red heat in a current of hydrogen.

If the temperature is too low, the reduced metal is pyrophoric, igniting and becoming re-oxidised by the oxygen of the air. The compounds of cobalt form valuable pigments. It unites with arsenic to form iron-grey, fusible and brittle compounds, when arsenic and cobalt are fused together. The alloy of cobalt and manganese is said to possess valuable properties. Cobalt may be deposited on metals by the electrolysis of a solution of the double sulphate of cobalt and ammonia ; and the deposit is said to be harder than that of nickel.

Cobalt, like nickel, is capable of uniting with carbon, and the porous cubes of metal may have the carbon removed by immersing in a permanganate of potash solution, drying and melting in a lime crucible. The carbon is oxidised, and when the metal begins to melt, a little aluminium or zinc is added to take up the oxygen.

Ores of Cobalt.—The principal ores of cobalt are : smaltine ($CoAs$), which is the most abundant ore, and frequently contains nickel and iron ; cobalt glance (Co_2AsS) ; and cobalt bloom ($Co_3AsO_4,4H_2O$). Cobalt is also often associated with nickel ores.

Oxide of Cobalt is prepared from cobalt speise by the wet way, as described under Nickel, and used for imparting a blue colour to glass, enamel, and pottery.

Smalt.—This is a double silicate of cobalt and potassium, also called cobalt glass. Its preparation is conducted in two stages : (1) the ore calcined to expel arsenic, sulphur, etc. ; (2) fused with sand and carbonate of potash, when it forms a deep blue glass.

Zaffre is an ore of cobalt containing sufficient silica to form smalt when fused with carbonate of potash.

Printer's Blue is used for painting the blue colour on pottery and china, etc. It is prepared by fritting a mixture of silica, oxide of cobalt, nitre, and a little barium sulphate.

CHAPTER XXIII.

ALUMINIUM.

WöHLER, in the year 1824, seems to have been the first to reduce aluminium, and later, in the year 1845, he obtained small globules by heating a mixture of potassium and aluminium chloride. Bunsen and Deville in 1854 independently obtained the metal by electrolysis of the fused chloride. Deville in the same year also prepared it in large quantities by using the natural mineral bauxite, which consists largely of alumina, associated with iron oxide. From this he produced aluminium chloride, and reduced it to the metallic state by means of potassium, which he replaced by sodium in 1855. Soon after this event, Dr. Percy and Rose obtained aluminium by the action of sodium on cryolite, but the metal was very impure. Deville turned his attention to the process, but found the double chloride of aluminium and sodium the better substance, using cryolite as a flux. This method continued to be the principal source of the metal until very recently, when the successful application of electricity to the reduction of aluminium compounds almost entirely replaced the chemical methods.

Aluminium, one of the most abundant of the elements, is a white metal, with a faint tinge of blue; it takes a fine polish, and its surface may be frosted like silver by plunging it for a short time in a weak solution of soda, swilling in water, and then digesting it in strong nitric acid. It is without odour and taste when pure, and the malleability increases with its purity, the best commercial aluminium being at least as malleable as silver. It yields easily to the hammer, bears distortion well, and can be flattened in two or three directions without cracking. Aluminium, like zinc, is most malleable at a temperature of from 100° to 150° C., but when rolled cold must be frequently annealed, as working

hardens the metal. If worked at a temperature exceeding
200° C., the metal becomes very red-short. Its elasticity and
tenacity are a little higher than that of silver. The frac-
tured surface is slightly fibrous, but on slow cooling it
becomes slightly crystalline. It is highly sonorous, emitting
a very clear sound. A bar of it suspended from a wire and
struck, gives out a high clear note, well sustained, and some-
thing like that produced from glass or porcelain.

Faraday noticed that the sound given out by an aluminium
bar is not limited to a single tone with its corresponding
upper tones, but there are two different tones audible—one
in the longitudinal and one in the transverse direction. This
is probably the reason why an aluminium bell, cast after the
usual pattern, has such a peculiar tone ; undoubtedly this
difficulty will be removed when the proper shape has been
determined. On account of its sonorousness and lightness,
aluminium is well adapted for wind instruments, drums, etc.,
especially for military bands, where the weight of the instru-
ments to be carried is quite an item. Its melting point is
625° C. Its conductivity is about 60 per cent. that of silver,
but very slight traces of certain impurities lower the con-
ductivity considerably. It is slightly magnetic and has a .
high specific heat. It is not easily volatile.

The extraordinary lightness of aluminium is best illus-
trated by the following table, comparing it with other
metals. A cubic inch of cast aluminium weighs 0·096 lb.

	Specific Gravity.	Weight per cubic ft. Lbs.	Volume per lb. Weight in cubic feet.	Relative Spec. Gr. Al=1.
Aluminium, . .	2·56	166·6	0·00625	1·000
Antimony, . .	6·72	420	0·00238	2·625
Zinc, . . .	7·15	437	0·00229	2·793
Iron, . . .	7·23	451	0·00222	2·824
Tin, . . .	7·29	455	0·00220	2·848
Steel, . . .	8	499	0·00200	3·125
Copper, . .	8·8	· 537	0·00186	3·437
Bismuth, . .	9·82	613	0·00163	3·830
Silver, . .	10·20	654	0·00153	4·000
Lead, . .	11·36	709	0·00141	4·438
Mercury, . .	13·60	849	0·00118	5·312
Gold, . .	19·40	1150	0·00087	7·578
Platinum, . .	21·50	1344	0·00074	8·410

It does not oxidise in air below its melting point when pure, but if its surface is rubbed with soft leather impregnated with mercury the surface becomes dull, and a white film of alumina soon appears. It does not combine with sulphur except at very high temperatures, and therefore is not affected, like silver, by sulphur compounds in the atmosphere. Nitric acid has little action unless it is concentrated and boiling. Dilute sulphuric acid is inoperative, but hydrochloric acid dissolves it readily. Vegetable acids have little action on it, and ammonia only slightly dissolves it. Solutions of potash and soda dissolve it readily, forming aluminates AlM_3O_3 and liberating hydrogen. Its chief impurities are silicon and iron.

It is used for many purposes, especially where lightness is important, such as telescope tubes, marine glasses, sextants, and scientific purposes generally, wire for lace, sword handles, culinary utensils, harness furniture, military equipments, purposes of ornament, and especially in alloys.

The following table of analyses is taken from Richards' *Aluminium:*

Commercial Aluminium.	Al.	Si.	Fe.	Cu.	Pb.	Na.
1. Parisian (Salvetat),	92·969	2·149	4·882	—	—	trace
2. Berlin (Mallet),	96·253	0·454	3·293	—	—	trace
3.	96·890	1·270	1·840	trace	—	—
4. Morin & Co., Nanterre (Sauerwein),	97·200	0·25	2·40	—	trace	trace
5. Parisian (Dumas),	92·500	0·70	6·80	—	—	—
6.	96·160	0·47	3·37	—	—	—
7. Parisian (Salvetat),	88·350	2·87	2·40	6·38	trace	—
8. Parisian from Haag,	92·000	0·45	7·55	—	—	—
9. Bonn (Kraut),	94·700	3·70	1·60	—	—	—
10. Morin & Co., Nanterre, 1862 (Kraut),	98·290	0·04	1·67	—	—	—
11.	97·680	0·12	2·20	—	—	—
12. (Hampe). The purest he could buy.	97·400	1·00	1·30	0·10	0·20	—
13. Wagner's Jahrb., 1887,	97·600	0·40	1·40	0·40	0·20	—

ORES.

Bauxite (see Refractory Materials) is a hydrated oxide of iron and aluminium with a little silica. Some varieties are white in colour, but generally they are light salmon to dark

red, according to the amount of iron oxide present. The light-coloured specimens are softer than the dark-coloured ones. It is somewhat difficultly soluble in acids, but fuses easily with acid potassium sulphate. *Cryolite*, $Al_2F_6,6NaF$, is a semi-transparent snow-like mineral found largely in Greenland. It is often associated with carbonate of iron, sulphide of lead, and silica, when it is red or black in colour. It is a readily fusible body, and is decomposed by sulphuric acid, yielding hydrofluoric acid. *Corundum* is an oxide Al_2O_3; and when coloured by other metallic oxides it forms ruby, sapphire, and emery. Native aluminium sulphate $Al_2(SO_4)_318H_2O$ occurs in New Mexico.

METHODS OF EXTRACTION.

Chemical Methods.—The Deville method consists of converting the ore, say bauxite, into sodium aluminate by fusion with sodium carbonate, which, being soluble, can be readily separated from iron, etc.,

$$Al_2O_3 + 3Na_2CO_3 = Al_2O_3,3Na_2O + 3CO_2.$$
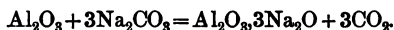
The liquor is next treated for the production of alumina by the action of a current of carbon dioxide, as shown in the equation $Al_2O_3,3Na_2O + 3CO_2 = 3Na_2CO_3 + Al_2O_3$; so that the sodium carbonate may be recovered by crystallisation. The alumina, after washing and drying, is mixed with common salt and charcoal and kneaded into balls, dried at 150° C., and transferred to vertical clay cylinders, which are covered with lids luted on, and placed in a suitable furnace and heated till all moisture is thoroughly expelled. The temperature is then raised to redness and a current of chlorine passed in, which decomposes the alumina and forms aluminium chloride thus :

$$Al_2O_3 + 3C + 6Cl = Al_2Cl_6 + 3CO.$$
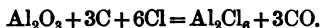
This chloride combines with the common salt. 400 lbs. of this double chloride, 200 lbs. of common salt, and 200 lbs. of cryolite, all perfectly dry and finely powdered, are placed in alternate layers, with eighty parts of metallic sodium, in clay or iron crucibles and gradually heated to redness ; the melted mass is then well stirred with an iron rod and the contents poured. About 20 lbs. of solid aluminium are obtained, and 5 lbs. in small globules mixed with the slag. If the crucibles are lined with calcined alumina, the metal is much freer from silicon, but is still contaminated with iron. Reverberatory

furnaces were afterwards used, the mixture being packed in sheet-iron baskets. The reaction is as follows:

$$Al_2Cl_6,2NaCl + 6Na = 2Al + 8NaCl.$$

On account of the low specific gravity of aluminium, there is a great tendency for some of the slag to remain with the metal. This may be removed by repeatedly heating the metal to redness in a plumbago crucible, when the scum rises to the surface and may be skimmed off. Copper and iron may be largely removed by fusion with nitre, and the fused portion allowed to liquate out. Zinc and other base metals are also oxidised. There is no good method generally known of removing silicon.

Mr. Castner in 1888 patented a cheap method of extracting sodium, which lowered the price of reducing aluminium. The old method consisted of a mixture of sodium carbonate, lime, and carbon in wrought-iron cylinders, and exposing it to a white heat, when sodium is evolved as vapour. The lime is added to prevent easy fusion, otherwise the carbon would rise to the top, float on the surface, and burn away. The new and cheaper method differs from the old, in working with a fused mass of soda compound and weighting every particle of carbon with iron, so that the carbon and sodium oxide are kept constantly mixed. By this means a soda compound may be employed which is decomposed at a lower temperature than can be used in the old process, and larger crucibles are admissible. The carbon-iron is obtained by coking pitch previously mixed with fine iron.

Aluminium by Electrolysis.—The reduction from the fused haloid compounds may be effected in a porcelain crucible by using carbon electrodes, or better, a carbon anode and a platinum cathode as used by Deville in 1854. In 1883 Gratzel patented his process, which consists of the electrolysis of fused aluminium chloride or fluoride, using an anode of compressed carbon and alumina. The melting pots were made of cast steel, and formed the cathode. The current was supplied from a dynamo. The metal obtained was impure, the material for the anodes was found to be impracticable, and great difficulties were experienced by polarisation of the cathode, which led to the discontinuance of the process.

In 1886 Dr. Kleiner of Zurich patented a process for electrolysing fused cryolite. The current was supplied in such a way that a small quantity of it generated heat, and kept the electrolyte in fusion while the larger proportion acted electrolytically. Powdered ore is packed round the carbon

electrodes in a vessel lined with bauxite, and a current of 100 volts passed through. The cryolite is fused by the arc, and becomes a conductor. The tension is then lowered to 50 volts, the quantity being about 150 amperes, and the operation continued till the bath is nearly exhausted. The metal obtained is contaminated with iron and silicon, unless pure materials are used. Dr. Kleiner found that the anodes rapidly wore away, while the ends which were immersed in the cryolite remained almost intact, while the 2 to 3 inches above was eaten away to the core. The new plan consists of submerging hollow cylinders of pure carbon in the melted cryolite, and connecting them with the positive current by means of projecting ears through the sides of the vessel; whilst the negative carbon is raised up through the bottom of the vessel until the apex is on a level with the upper part of the hollow carbon cylinder. The powdered cryolite is
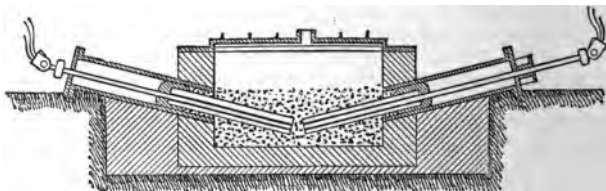
Fig. 137.

then fed in, and the first fusion effected by forming an arc between the negative carbon and one long carbon rod suspended from the top, used only for this purpose, and which can be moved in any direction by the hand, so that the cryolite around the two poles may be melted. The positive rod is slowly moved across the vessel, toward the hollow carbon cylinders at the sides, until the current flows freely through the melted cryolite between these and the negative carbon in the centre. This requires ten minutes, when the carbon rod is withdrawn, and the electrolytic process then carried on. These hollow cylinders are little affected, and may be used for many operations.

Cowles's Method.—Aluminium and its alloys are prepared by the Cowles's Electrical Smelting Company in an electrical furnace, represented in vertical section in Fig. 137. It consists of an oblong receptacle, the internal dimensions being 5 feet long, 3 feet 3 inches deep, and 20 inches wide.

It is built below the floor line, and lined with fire-bricks. Into the ends are built cast-iron tubes, inclined, as shown, for convenience in working the electrodes. On the covers are screwed blocks of wood surrounding the bosses. Near the outer ends of the electrode rods are easily removable clamps, each of which holds a nut, through which passes a screw having a T handle at its outer end, whilst its inner end rests against the wooden block. The rotation of this screw moves the electrode inwards or outwards. The top of the brickwork is covered with iron plates, and an iron cover is placed over the mouth of the furnace. In the cover is a hole, through which the gases issue as they are driven off by the heat in the furnace. The electrodes consist of carbon rods $2\frac{1}{4}$ inches in diameter, and nine of them are attached to each electrode rod. The attachment, as shown in the figure, consists of metal, which is cast round the ends of the carbons and of the electrode rod so as to form a conductor, which is in perfect contact with the whole of the parts connected.

The application of the furnace is as follows: The two electrode rods are connected to the two leads of the dynamo, the cable joining the positive pole sending the current into the left hand electrode, whence it travels through the charge, where it meets with the resistance which causes the heat, and passes by way of the right-hand electrode into the cable connected to the negative pole of the dynamo. Resistance is caused by the particles of the carbon which are mixed in the charge. Thus the current acts independently of the structure of the furnace itself, acting simply on the charge, which is in immediate contact with the carbon, by means of which the heat is produced.

The ore employed is sometimes corundum, also called emery. The dull crystals are termed corundum, and the grey and black varieties emery. It is essentially alumina Al_2O_3. At the present time the ore employed in England is bauxite. The charge, while being inserted, is prevented from spreading out laterally by two pieces of sheet-iron connected by a distance-piece, and placed one on either side of the electrodes; the charge is put in between them, and charcoal is then filled in between the sheet-iron and the sides of the furnace, after which the sheet-iron is withdrawn, the top of the charge covered, and the ends of the furnace filled with charcoal to the depth of a few inches above the charge and the electrodes. The iron cover is then luted on with fire-clay. A current of 2000 to 3000 amperes is applied at first, and as the charge becomes fused the resist-

ance diminishes. The electrodes are then drawn further
apart, the speed of the engine increased, and a current of
5000 amperes flows through the charge, until the whole of
the ore and metal is fused. One operation requires about
one hour and three-quarters. This furnace is chiefly used in
the production of aluminium alloys. The charge for copper
alloys consists of 300 lbs. of materials, about one-fourth being
aluminium ore broken up small, a good deal of which is
supplied by broken-up slag taken from a former heat,
about 4 per cent. of carbon, and the balance is granulated
copper.

Heroult's Process (1888).—This method, like that of Cowles,
depends on the enormous temperature of the electric arc
which melts the alumina, and the high temperature of the
furnace, assisted by the carbon, probably effects its reduction
to the metallic state. The process was first put into opera-
tion at Neuhausen, and consists of electrolysing or reducing
alumina in contact with copper or other metals, forming
alloys. The anode is hard carbon and the cathode a layer of
copper or iron. Water power from the Rhine Falls is used
for driving the dynamo. The crucible is made of carbon
contained in one of plumbago, and the ore mixture is cryolite
and alumina. The inner crucible serves as a cathode ; it is
provided with a lid having two holes, through one of which
connection is made by a carbon rod with the crucible, and
through the other another carbon rod dips into the middle
of the bath. To form copper alloys the metal is melted in
a carbon crucible by a voltaic arc, the anode being a
movable carbon rod, and the copper serves as the cathode,
connection being made with the crucible. When the copper
is melted the alumina is introduced and is also soon liquefied
and decomposed.

Hall's Process.—This was patented in 1889 and consists of
dissolving alumina in a fluid bath of double fluoride of
aluminium and potassium, and electrolysing the same with
an anode of non-carbonaceous material. The anode is of
copper or platinum, and the cathode of carbon. A low red
heat is sufficient for carrying on the operation. Aluminium
and calcium fluorides are also used. At the Pittsburg Re-
duction Works two dynamos in parallel are used, producing
a current of 20 volts and 1700 amperes. Two reducing pots,
coupled in series, are used. Each pot is of cast iron, lined
with carbon, which forms the negative electrode, while a
number of carbon rods suspended in the bath form the
positive electrode. Each pot is 24 by 16 by 20 inches, and

holds 300 lbs. Nearly the whole of the aluminium in a given charge is extracted in one operation. If it is desired to make alloys, the metal to be alloyed with aluminium takes the place of carbon as a cathode. It will be seen then that in this process alumina is dissolved in a suitable solvent and electrolysed without the solvent being itself decomposed.

The following notes with reference to the industrial treatment of aluminium may be useful. In consequence of its softness, aluminium tears and clogs under a cutting tool. In order to prevent this, it is advisable to take small cuts, and to keep the work well oiled. Single-cut files work better than cross-cut, and when they become clogged may easily be cleaned by dipping them into a solution of caustic soda and washing in hot water. In many cases, grinding on a soft grained stone is better than filing. Aluminium may be polished with an ordinary chamois skin or rag buff, and burnished either with a steel burnisher or piece of soft wood, using olive or vaseline oil. Aluminium can be coined, stamped, or spun very easily, but soap water should never be used ; the best substitute is a mixture of four parts oil of turpentine and one part of stearic acid. The same mixture should be used in graving. The temperature for annealing should not exceed 200° C. The proper heat is reached when a pine stick, drawn across the surface of the metal, leaves a brown streak. Small objects may be annealed by heating in oil.

Melting and Casting.—Aluminium may be melted in an ordinary graphite crucible without taking up silicon from the walls, provided it is done *without* a flux and at a low heat. It may also be melted in small quantities in an iron ladle, but great care must be taken not to get it too hot. On account of its high specific and latent heats, aluminium requires a long time to melt; but, unlike many other metals, it does not require to be heated far above its melting point to become fluid enough to pour into moulds. It can be cast either in metallic moulds or in sand. If in the former, the mould should first be heated and covered with a suitable coating, then thoroughly dried and again heated before using. If in sand, care must be taken that the mould is perfectly dry. In either case the moulds should be provided with many vents, and have the gates as nearly round as may be. The exact temperature at which the metal is to be run can only be ascertained by experience ; if the castings produced are hard and brittle, the metal has been too hot, whilst

blisters indicate that the temperature has been too low when pouring. If the castings are required to be very hard, or to be plated with gold, silver, etc., then 1 to 2 per cent. of tin is added.

Frosting.—For producing a fine white frosted appearance, like that of frosted silver, immerse the aluminium in a heated solution of potash. A fine matt can be obtained by acting on the metal with a weak solution of caustic soda, washing well in water, and afterwards dipping into a strong solution of nitric acid. Articles treated in either of these ways preserve their original beauty for years.

Plating.—In order to plate aluminium with gold, silver, etc., it is necessary first to cover it with a firm coating of copper. The current must be regulated in such a manner that only very small bubbles appear on the aluminium ; as soon as the bubbles get too large, the coating becomes imperfect, and the current has been too strong. After obtaining a perfect coating of copper, in the manner described, which may be brushed or polished, or simply dried, the articles may be silvered, gilt, bronzed, or brassed, etc., in the ordinary way.

Soldering.—Aluminium is so easily oxidised at a soldering temperature, and the oxide is so insoluble in ordinary fluxes, that the thin film of oxide, which is continuous and unalterable, protects the metal underneath it from further oxidation. This film of oxide acts effectually in preventing any other metal from coming in close enough contact with the aluminium beneath it, and thus soldering is prevented. Almost every possible chemical re-agent has been tried as a flux by scores of inventors, but up till recently none had been found practicable. Professor Richards has come to the conclusion that the solder should contain its own flux, so that the instant the film of oxide was removed, the solder proper would be simultaneously present to take hold of the aluminium surface at the same instant that it was cleansed from oxide. In using the solder it is necessary that the parts to be joined shall be scraped or filed clean immediately before soldering. The edges should be heated and the stick of solder rubbed on them until every part is coated or tinned with a thin layer of the solder. In this heating a clean flame is absolutely necessary, as a prime factor in these operations is cleanliness, and any soot or other dirt will probably defeat the object in view. For a lap joint the edges are then brought together, the soldering iron passed along, and a little extra solder melted along the edge of the

joint. For a joint at an angle, it is necessary that the iron be shaped to fit, so as to get it well into the corner, for the solder is not likely to adhere well, except where it is rubbed in with the iron. The tinning of the edges can also be done with the iron, by first tinning the clean iron with the solder, and then rubbing the solder strongly on the freshly scraped surfaces. In joining aluminium with a lock joint, the edges of the sheet should be coated with the solder before it is turned over, or else the solder will not soak into the joint.

CHAPTER XXIV.

MERCURY OR QUICKSILVER.

THE chemical name is Hydrargyrum ; its symbol is Hg, and its atomic weight 200.   This metal has been known from the earliest times.   Cinnabar was used by the ancients as a pigment, and the chlorides of mercury by the alchemists.

Mercury has an almost silver-white colour, and in extremely thin films transmits a violet light ; it is liquid at the ordinary temperature.   At 360° C. it boils, forming a colourless vapour having a density of 100, and corresponding to the molecular weight of 200.   Its molecule appears to contain only one atom at that temperature.   Mercury gives off vapour even below 40° C.   Its specific gravity is 13·59, and its specific heat is ·032.   Its conductivity for electricity is $\frac{1}{7}$ that of pure silver.   It contracts uniformly when cooled to the solidifying point, and at − 39° C. it freezes, contracts considerably, and forms a tin-white, ductile, malleable and crystalline metal of specific gravity 14·2.   It has a high and fairly regular co-efficient of expansion for heat, which renders it eminently suitable for thermometers and similar instruments.

It is not affected by air or oxygen at ordinary temperatures, so that impurities may be detected by shaking the metal in a bottle for some time, when base metals will be oxidised and discolour the mercury.   If heated to near the boiling-point it oxidises, forming the red oxide HgO, but at a higher temperature this oxide is decomposed into mercury and oxygen.   When mercury is agitated with ether, sugar, turpentine, oils, sulphides, chalk, etc., a grey powder is formed consisting of small globules of mercury and a little oxide. This is known as " deadening," and is used in the preparation of ointment, pills, etc.   This deadening or sickness of mercury occasions great loss in amalgamation processes for extracting gold and silver.   Mercury combines with gold, silver, tin,

lead, bismuth, cadmium, copper, and zinc, but less readily with iron, to form amalgams. Hydrochloric acid has no action on mercury, nitric acid dissolves it, and strong sulphuric acid when warmed attacks it with the evolution of sulphur dioxide. Aqua regia converts it into chloride, and the same occurs with chlorine gas. Bromine, iodine, and sulphur vapour also dissolve it.

The commercial metal is frequently contaminated with certain other metals, such as zinc and bismuth, which distil over with the mercury in its extraction. Lead, antimony, tin, bismuth, have been added as adulterations. The comparative purity of mercury may be tested by forcing it through chamois leather or by filtering through blotting paper, when no stain should be left behind. Or by shaking in a bottle of air as before mentioned. Or by allowing it to roll down a slight incline, when a tail is formed if impure, instead of rolling as a perfect sphere. Mercury is best purified by re-distillation. The chief uses of mercury are in amalgamation methods for the extraction of gold and silver; for the construction of philosophical instruments, as thermometers, barometers, etc., for the manufacture of vermilion and other mercury compounds, and to some extent for gilding and silvering looking-glasses, etc.

The method of gilding by means of mercury is termed "water gilding," and was much in use before the introduction of electro gilding. The gold is formed into a fluid amalgam, pressed through wash leather, and placed on the previously cleaned article and well rubbed until a firm, coherent surface is obtained. The mercury is then expelled by heat and the surface finally polished or burnished. The silvering of mirrors may be effected by coating one surface of the glass with an amalgam of tin and mercury. The amalgam is spread on the perfectly flat surface of a sheet of tinfoil placed on a table which can be rotated and inclined at any desired angle. The clean glass is then pushed forward over the amalgam so as to exclude air bubbles and superfluous mercury, and then weights or pressure are put on to make the metals adhere.

Vermilion.—Mercury forms an important compound with sulphur, mercury sulphide HgS, which may be prepared by gradually adding 200 lbs. of mercury to upwards of 32 lbs. of molten sulphur in an iron pot, with constant stirring. The mass is poured on to an iron slab, then broken up when cool and heated in clay crucibles and sublimed out of contact with air, when it has a beautiful rich colour. If it is heated with access of air it is decomposed, mercury and sulphur dioxide

being formed. It is also decomposed by carbon, iron, and most metals. Also by lime, oxide of iron, alkalies, and by hydrogen gas. Nitric acid has only a feeble action on it in the cold, while aquafortis dissolves it readily. If boiled in water with metallic zinc mercury is liberated, and the same occurs with copper to a limited extent. Barium sulphide readily dissolves it.

Mercury and chlorine combine in two proportions—*Calomel* Hg_2Cl_2, is prepared by adding a chloride to the solution of a mercurous salt, or by adding mercuric chloride and alcohol to mercury and rubbing till the mass is deadened. The mixture is then sublimed, and the calomel condenses as a solid, translucent, fibrous cake. Mercury sulphate, common salt, and mercury, when rubbed together and the mixture heated, also produce calomel. Calomel is a heavy, white, tasteless powder, insoluble in water, alcohol, or dilute nitric acid, and is largely used in medicine. *Corrosive Sublimate*, $HgCl_2$, is a white or colourless, translucent, crystalline body, which is soluble in water and alcohol. It is a very powerful poison. It is formed when chlorine or aqua regia dissolves mercury. On the large scale it is formed by distilling a mixture of mercuric sulphate and common salt :

$$HgSO_4 + 2NaCl = Na_2SO_4 + HgCl_2.$$
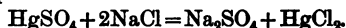
Mercuric chloride is reduced by heating with most metals, forming mercury and amalgams.

Ores of Mercury.—Mercury occurs native as globules in Spain, Hungary, Sweden, America, etc. Also in some places as amalgams of silver and gold. The most important ore is the sulphide or cinnabar, HgS. It is a brownish-red (transparent when pure) mineral, massive, crystalline, and fibrous, with a scarlet streak and a hardness of 2 to $2\frac{1}{2}$. The crystals are sectile, breaking with a partially conchoidal fracture, and having a specific gravity of about 8. It is often nearly pure, and occurs in Germany, Austria, Russia, China, Japan, Mexico, Peru, California, and Spain. Horn quicksilver, Hg_2Cl_2, is a greyish-coloured ore, massive and crystalline, with a yellowish streak. Iodides and bromides are rare. Selenides mixed with sulphides of a steel-grey or lead-like colour are occasionally met with.

EXTRACTION OF MERCURY.

The methods of extraction are based on the decomposition of mercury compounds by heat with the volatilisation of

sulphur, etc., and distillation of the mercury. The sulphur may be oxidised by air or absorbed by lime—forming calcium sulphide and sulphate—or by ignition with lime and oxide of iron. The first method is generally employed. The quality of the ores employed varies considerably from 75 per cent. to ·5 per cent. The ore roasted averages 1·5 per cent. The finest ores are powdered, mixed with quicklime, pressed into bricks, and roasted for four to five hours in muffle furnaces. Coarser ores are roasted in reverberatory furnaces, such as the Alberti furnace. The materials treated are divided into "smalls, sands, and ores," the smalls containing the least, and the ores the most mercury.

1. **Air Reduction.**—The mode of decomposition may be represented by the equation $HgS + O_2 = SO_2 + Hg$. At Almaden, in Spain, the reduction chamber is a "dome" furnace, with an opening near the top communicating with a system of earthenware condensers called

Fig. 138.

"aludels" (Fig. 138), each about 18 inches long and arranged upon two slopes of brick-work. The uncondensed products pass into a chamber containing a cistern of water. The furnace is heated with a wood fire, and when the necessary temperature is attained, the fire is withdrawn and air admitted. The sulphur dioxide and mercury pass through the long chains of aludels, and the mercury is condensed.
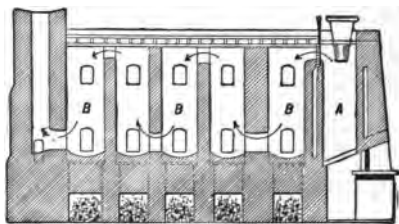
Fig. 139.

In the great Idrian works a furnace 180 feet long and 30 feet wide, with the fire-place in the middle and condensing arrangements similar to that of Fig. 139, was formerly exclusively used. Hähner introduced a modification at New Almaden, California, because this furnace requires to be stopped for five days after working off a charge.

The Hähner furnace (Fig. 139) consists of a vertical cylinder

(A), 18 feet high and 3 feet 8 inches in diameter, into which the ore is fed from a hopper; there are six condensing chambers (BB), the roofs of which are covered with an iron plate, which forms the floor of a tank through which water is kept circulating. The vapours are compelled to pass in the direction of the arrows, the communication between the chambers being alternately at top and bottom. The current is maintained by a chimney draught built in three tiers, in each of which are ledges kept cool by water flowing over them so as to complete the condensation. The charge consists of 7 cwts. ore with 5 per cent. of charcoal. The furnace is worked continuously.

*Hüttner and Scott** have lately introduced a furnace termed a monitor or ironclad, in which fine ores can be treated continuously. This furnace is hexagonal in plan at the base, and three fire-places burning wood as fuel are arranged round it. Above these the shaft is cylindrical. At the top is the vapour chamber, which conveys the fumes to the condensers through iron pipes. The furnace is 11 feet high and 6 feet wide. The charging is effected by a cup and cone arrangement, with an apparatus at the top for keeping it hermetically sealed while the cone is being lowered. As a portion of ex-
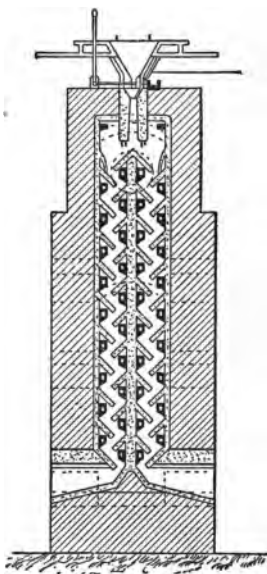
Fig. 140.

hausted ore is removed from the bottom, fresh ore is added at the top. The air for combustion is heated by passing through a clay pipe in the condensers, and branch pipes also supply hot air to the fires and prevent too much soot. The peculiar feature of this furnace is the ore chamber (Fig. 140), 27 feet high and only 25 inches wide and 11½ feet long. They are built in pairs. On opposite sides of the interior are tiles inclined at an angle of 45°, and similar ones

* Thorpe's *Dict. of App. Chem.*, Vol. II., p. 560.

in the centre, so that the ore falls from one to the other, and exposes a large surface to the hot air from the furnace, which enters through a number of holes and carries the mercury vapours to the condensers. It is necessary that the vapours should enter the condensers at about the boiling point of mercury.

Condensation of Mercury.—Iron condensers are useful in cooling the vapour to near the boiling point of water ; at a lower temperature the condensed acid vapours corrode the iron. Brick chambers are also gradually acted on, and thin glass is used when the vapours are comparatively cool. Brick chambers gradually get hot and cool very slowly, so that they cannot be used continuously. At Idria and some other places iron condensers coated with asphalte and surrounded with water are used, the vapours finally passing into water. In the case of the monitor furnace they pass to the off-take at
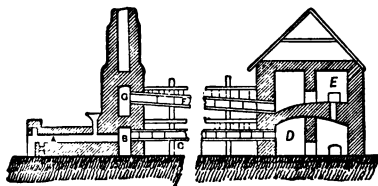
Fig. 141.

350°-400° C., and enter the first condenser at 200° C., and when they enter the third brick condenser the temperature is reduced to 40° C. They leave the glass condenser at 14° C. and then pass into the chimney. The sooty deposit on the walls of the condensers is removed and rubbed with wood ashes to brighten the metal, which amounts to about 5 per cent of the total in the ore. The residues are roasted with fresh ore.

The Alberti furnace (Fig. 141) is employed for "smalls" and poor ores containing about 1 per cent. of mercury. It consists of a reverberatory furnace (A) capable of holding 3 tons, with a sloping bed arranged in three steps, the ore being gradually pushed forward from the flue end to the fire bridge ; the vapours pass into a condenser (B), and thence along the iron tubes (C), then into a condenser (D), up into (E), then back through tubes (F) into a chamber (G) at the base of the chimney, which is obstructed by a number

of partitions, around which the vapours pass so as to condense any remaining mercury. The iron pipes (c and F) are kept cool by running water. This furnace is worked uninterruptedly for six months when the pipes have become coated with a deposit containing 40-50 per cent. of mercury.

Closed retorts were also formerly employed for mercury ores, using lime, iron, or oxide of iron as the reducing agent, when the following reactions occurred :

$$4HgS + 4CaO = 3CaS + CaSO_4 + 4Hg$$
$$HgS + Fe = FeS + Hg$$
$$5HgS + Fe_3O_4 = 3FeS + 5Hg + 2SO_2.$$
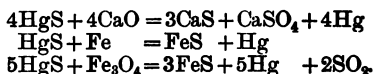
Purification of Mercury.—Mercury is purified from zinc, bismuth, antimony, and tin, which are its chief impurities, by placing it in a retort, covering with iron filings, and distilling the mercury, which is condensed by the leading pipe dipping in water. The metal is collected and treated with hydrochloric acid, washed with water and carefully dried at a gentle heat. Instead of iron as above, it is better purified by adding $\frac{1}{10}$th its weight of cinnabar and then re-distilling. The mercury sulphide is decomposed, and the metals existing as impurities unite with the sulphur and remain behind.

Certain wet methods are also employed. Sulphuric and nitric acids are used, but these will not remove gold or platinum. Equal weights of mercury and strong sulphuric acid are mixed together and the metal repeatedly shaken or stirred for hours or days according to the amount of impurity, fresh acid being added as required. The action is continued as long as the acid shows any turbidity due to the separation of base metals. Dilute nitric acid, mercurous nitrate solution, and ferric chloride solution are also used for purifying mercury.

CHAPTER XXV.

ANTIMONY, ARSENIC, AND BISMUTH.

ANTIMONY.

THIS name is derived from the French *Antimon*. It is termed *Stibium* in the German. Its chemical symbol is Sb, and its atomic weight 120. It is a bluish-white metal with a brilliant lustre, highly crystalline and brittle, with a specific gravity of 6·7 to 6·86. It crystallises in the rhombohedral system, and the surface of the metal exhibits characteristic fern-like markings. Absolutely pure antimony is said to crystallise only with difficulty. Antimony expands on solidifying, and imparts this property to most of its alloys ; but, according to Duflos, pure antimony does not expand on solidifying. Its specific heat is ·051, and its coefficient of linear expansion ·0000105. It melts at a temperature of 440° C., and at temperatures but little removed from its melting point it slowly volatilises. It boils at a white heat, and may be readily distilled in an atmosphere of hydrogen. It is a poor conductor of heat and electricity.

It does not oxidise at ordinary temperatures ; but when heated in air, and especially when melted, it rapidly oxidises, producing white fumes of the trioxide, Sb_2O_3. At a red heat it burns in air with a bluish-white flame, forming the dense white fumes of the trioxide. Antimony is capable of existing in two forms—the ordinary or crystalline form, and the amorphous form, which is explosive.

The latter is prepared by passing a weak electric current through a concentrated acid solution of antimony trichloride. When heated above 77° C., and struck, or scratched, it rapidly changes to the crystalline variety with the production of great heat. The amorphous form contains antimony chloride,

and probably hydrogen in the occluded state. Powdered antimony ignites when thrown into chlorine or bromine vapour. Antimony is precipitated from its acid solutions by zinc in the form of a fine black powder, and used for producing the appearance of steel on papier-maché and plaster ornaments, etc.

Antimony and sulphur readily unite when heated together, forming the trisulphide, Sb_2S_3. The same compound is also formed by heating the oxide with sulphur :

$$2Sb_2O_3 + 9S = 3SO_2 + 2Sb_2S_3.$$
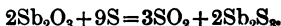
Sulphuretted hydrogen precipitates the same compound when passed into an antimony solution. It then has an orange colour, but, when formed in the dry way, it is a bluish-grey crystalline compound with a metallic lustre. When this sulphide is roasted in air, a mixture of Sb_2O_3 and Sb_2O_5 is produced with the liberation of sulphur dioxide. The sulphide is partly decomposed by carbon at a high temperature, and at a red heat it is completely decomposed by iron and the alkali metals, also by a mixture of potassium cyanide and carbonate. When steam is passed over the sulphide an orange-coloured body sublimes, containing trioxide and sulphide of antimony. This sulphide may be oxidised by fusion with nitre.

Glass of Antimony.—When antimony sulphide is partly roasted and then fused with a little sulphur, it forms a glassy mass of a yellowish-red to hyacinth-red colour.

Livers of Antimony is a brownish-black crystalline sulphantimonite of potassium, prepared by fusing antimony sulphide with potassium sulphate and charcoal.

Ores of Antimony.—These are found in the Harz, Borneo, Hungary, Bohemia, France, Sweden, United States, Canada, Australia, Cornwall, etc. In addition to the ores proper, antimony very often accompanies copper, lead, zinc, silver, and other ores in different parts of the world. Native antimony is often found alloyed with arsenic, nickel, silver, and sometimes iron, but the chief ore is stibnite (Sb_2S_3), or grey antimony ore. An oxysulphide known as antimony blende or kermesite, $Sb_2O_3,2Sb_2S_3$, is found. Some sulphides contain considerable quantities of gold. Antimony bloom, Sb_2O_3, and antimony ochre, Sb_2O_4, are other ores. Arsenical antimony is a mixture of arsenic and antimony ores.

METHODS OF EXTRACTION.

Sulphide of antimony occurs in a mass of rocks, from which it may be largely separated by liquation ; but poor ores cannot be treated in this way. Also very rich ores are smelted direct.

The liquation was formerly effected in the Harz by placing the ore in conical pots, covered at the top, perforated at the bottom, and standing on receivers sunk in the ground; the space between the pots is occupied by the fire. The fused sulphide runs through the perforations, and collects in the receivers placed below. At Malbose, in France, the ore was placed in large cylinders (A) (Fig. 142), perforated at bottom, each holding 500 lbs., four being placed in one furnace, and standing on perforated plates (B), beneath which were chambers containing earthen receivers for the liquated material. At Linz, the liquation is performed in a reverberatory furnace, the bed inclining towards the tap hole, through which the liquated sulphide flows into a receiver placed outside.
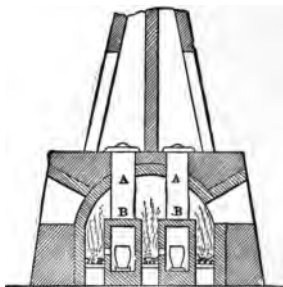
The reduction of the sulphide in England is performed in large crucibles heated in circular wind fur-

Fig. 142.

naces. Each crucible is charged with 40 lbs. of sulphide and 20 lbs. scrap iron, the product being impure antimony and sulphide of iron, thus : $3Fe + Sb_2S_3 = 3FeS + 2Sb$.

The sulphide may also be reduced by mixing it with small coal to prevent caking, and roasting at a gentle heat in a reverberatory furnace, when a mixture of sulphide and oxide results. This is then mixed with ·5 part of cream of tartar, or 1 part charcoal and ·5 part potash, and fused in a crucible. The slag is an alkaline carbonate mixed with double sulphide of antimony and potassium, and is known as *crocus of antimony.* The products are metal, regulus, and slag. The metal is purified by fusion with nitre, or by melting and stirring with an iron bar.

On account of the volatility of antimony, ores containing

less than 25 per cent. of antimony can only be profitably
worked under special circumstances.   A rich ore contains
65 to 68 per cent. of antimony.   The relative purity of refined
antimony is judged by the length and form of the star or
fern on the surface of the ingot.   Very small quantities of
certain impurities prevent it from starring, hence the trade
term of star antimony for metal of high quality.   A small
quantity of tin in antimony is said to produce large crystals.
The following analyses show the composition of crude
antimony :

Antimony,* .	.	.	.	94·5	84	97·2	95
Iron, .	.	.	.	3	10	2·5	4
Sulphur,	.	.	.	2	5	0·2	0·75
Arsenic,	.	.	.	0·5	1	0·1	0·25

The crude metal may be freed from small quantities of
sulphur, arsenic, copper, and iron by fusing it with 1 part
sulphide of antimony and 2 parts carbonate of soda, and then
repeating the fusion with carbonate of soda alone.   Carbon
and similar reducing agents must be absent.   Copper and
iron may be removed by fusion with nitre.   Pure antimony
may be obtained by heating tartar emetic to low redness and
digesting the mass in water to remove potassium.

By oxidising impure antimony in nitric acid and filtering
off the precipitated oxide, then drying and heating with
charcoal in a crucible, the metal is reduced.   By this method
the arsenic is dissolved and separated.   Pure antimony may
also be deposited from a solution of antimony sulphide in
sodium sulphide by means of an electric current.

Borcher † has proposed to extract antimony from its ores
by dissolving them in a solution of sodium sulphide, adding
an excess of sodium sulphide, but not enough to form a
saturated solution.   So much of the antimony sulphide is
dissolved as will make a solution of the specific gravity of
1·09 or 12° Baumé.   3 per cent. of sodium chloride is then
added to increase the conductivity.   The vessels are made
of iron, which form the cathodes, and the anodes are made
of lead.   A current of 2 volts per vat is used for each vessel,
and nearly all the metal is deposited out of the solution.   It
is washed with soda, and then with weak hydrochloric acid,

* Thorpe's *Dict. of App. Chem.*, Vol. I., p. 182.
† *Jour. of Soc. of Chem. Industry*, Vol. VI., p. 673.

and lastly with water. It is then dried and melted with glass of antimony as a flux.

ARSENIC.

The compounds of this element have been known from very early times, chiefly the sulphide and oxide. In small quantities it is very widely distributed over the earth, sometimes native, but more generally in combination with pyritic and other ores. In England it is chiefly found with tin ores, and on the Continent in mispickel.

Arsenic is a very brittle metal, of a steel-grey colour and bright metallic lustre. Its specific gravity is 5·67, and it crystallises like antimony in rhombohedrons. It is a comparatively poor conductor of heat and electricity, and is without odour or taste, but when burnt in air the odour of garlic is perceived, and a yellow vapour is formed. At a dull red heat it volatilises without fusion, but when heated under pressure it liquefies at 500° C. Above 200° its vapour is phosphorescent. When the vapour of arsenic is condensed at a temperature a little below its volatilising point, it scarcely oxidises in air, even when heated to 80° C. When it is condensed on a cold surface and not completely surrounded by its own vapour, it solidifies as a dark-grey crystalline powder, which is readily oxidisable.

When arsenic is heated in air it burns with a blue flame, producing arsenic trioxide, As_2O_3. In pure water it is unaltered, but when exposed to air it forms a grey powder, which is probably a mixture of metallic arsenic and its oxide; this is used as a fly-powder. If arsenic is sublimed in a stream of hydrogen and condensed at 215° C., a vitreous variety of arsenic is formed, having a specific gravity of 4·7. At 360° it is converted into the crystalline form with evolution of heat. When heated with sulphur it forms a red compound termed realgar, As_2S_2. Another sulphide, As_2S_3, known as orpiment occurs native, and is artificially prepared by subliming arsenic trioxide with sulphur. It is yellow in colour, and has a resinous lustre. Arsenic combines with chlorine, bromine, and iodine. Its atomic weight is 75. It is a constituent of several alloys; it is used for bronzing glass and in the manufacture of opal glass; it is burned in oxygen as a signal light in trigonometrical surveys.

Ores of Arsenic.—Native arsenic occurs in reniform

and stalactitic masses associated more or less with iron,
cobalt, nickel, antimony, and silver in Siberia, Saxony,
Bohemia, Transylvania, Norway, and the United States.
Realgar, As_2S_2, and orpiment, As_2S_3; arsenical pyrites or mis-
pickel, $FeS_2,FeAs_2$; kupfer-nickel, Ni_2As and $NiAs_2$; white
cobalt, $CoAs_2$; cobalt glance, $CoS_2,CoAs_2$; nickel glance,
$NiS_2,NiAs_2$, are some of the forms in which arsenic occurs,
besides being associated with a great number of other ores.

Extraction.—Arsenic is usually obtained from native
arsenic and mispickel in earthenware retorts laid horizontally
in a furnace. The retorts are 4 to 5 feet long, made of fire-
clay, and glazed inside with a mixture of oxide of iron, alum,
blood, and loam, so as to render them impervious. A sheet-
iron pipe is joined to the mouth,
and to this is luted a clay con-
denser. On the application of
a moderate heat the arsenic sub-
limes and condenses largely in
the iron tube as a compact, grey,
crystalline mass.

The white oxide (As_2O_3) called
arsenious acid exists in the amor-
phous and crystalline forms. It
is obtained from the calcination
of many ores containing arsenic,
forming transparent masses called
arsenical glass. It is purified by
resubliming in deep iron vessels
(Fig. 143), and collecting the
vapours in a divided condensing

chamber. When heated with
carbonic oxide, or hy-
drogen below redness, it is reduced to metallic arsenic, thus :

$$2As_2O_3+3C=3CO_2+4As.$$
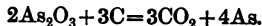
Arsenical Glass is prepared by volatilising the whole
powdery trioxide under pressure in a retort such as in
Fig. 143.
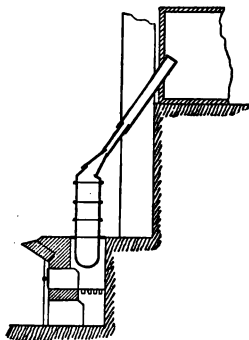
BISMUTH.

This metal is but sparingly distributed over the earth ;
the principal localities where it occurs are Adelaide, Alten-
berg, Saxony, Carinthia, Sweden, and Bolivia. It is also

found in Cumberland and Cornwall associated with ores of nickel.

Bismuth is a white metal with a tinge of red, and bright metallic lustre. It is crystalline and brittle, a bad conductor of heat and electricity, and possesses a low tenacity. The crystals are rhombohedral. It melts at 268° C., and boils at about 1200° C.; its specific gravity is 9·80, but unlike most other metals this is diminished by pressure, according to Scheerer. Spring, however, has shown that at a pressure of 20,000 atmospheres the density is increased to ·9·86, and it is stated that by careful hammering the density is in-creased. The density of bismuth is greater in the liquid than in the solid state. Wrightson and Austen gave it as 10·05. Bismuth is said to expand on cooling, but Tribe states that this expansion does not occur until after solidi-fication. Bismuth is the most strongly diamagnetic body known. When comparatively pure the metal crystallises readily. This may be shown by melting it in a crucible, and when a crust has formed on the surface by piercing it with a hot iron rod the liquid in the interior may be poured out; the inside will then be coated with obtuse rhombohedral crystals. Metallic iron, copper, lead, or tin precipitate metallic bismuth from its solutions.

When heated in air it readily oxidises, and at higher temperatures burns with a bluish flame, emitting yellow "*flowers of bismuth*," Bi_2O_3. This oxide melts at a red heat and forms a glass, which is used in glass and porcelain staining, and with gold in gilding porcelain. If a trace of silver is present, it darkens on exposure to light. It is reduced by heating with carbon. Bismuth and sulphur unite at a red heat, forming Bi_2S_3, which is a dark-grey crystalline solid with metallic lustre. Bismuth oxide has the power of dissolving other oxides, and may replace lead in the process of cupellation.

Ores of Bismuth.—Native bismuth is found massive, granulated, and arborescent, associated with silver, iron, arsenic, etc. Bismuth glance, Bi_2S_3, bismuth ochre, Bi_2O_3, and bismuthite, which contains carbonates of iron and copper, are the chief ores. Native bismuth was formerly separated by liquation, but is now largely extracted by smelting processes. Reference has been made to this in treating of the Freiberg scheme for lead, silver, etc., p. 226.

EXTRACTION OF BISMUTH.

When bismuth is separated from its ores by liquation, the furnace employed is similar to that shown in Fig. 144. It contains a series of iron tubes inclining towards the front, in which the ore is placed. The fire-place is below, wood fuel being employed. The liquated metal is received in iron pots kept hot by a separate fire. The tubes are charged from the upper end with about 56 lbs. of ore, and if they are hot with a previous charge the metal will begin to flow in a short time. A temperature but little above the melting point of bismuth is needed, and the flow of metal is facili-
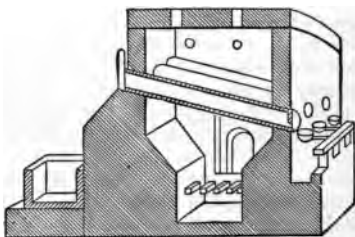
Fig. 144.

tated by stirring the ore from the upper end with a small rake.

Sulphur ores of bismuth are first roasted to remove the sulphur and volatile matters as far as possible, then smelted in crucibles with iron and carbon, using carbonate of soda as a flux, and producing metal, regulus or speise, and slag. Ores containing much copper may be smelted with an alkaline flux and free sulphur, so as to form copper regulus and impure metallic bismuth. The impurities generally found in crude bismuth are: silver, lead, copper, sulphur, arsenic, antimony, nickel, cobalt, and a trace of iron. Sulphur and arsenic may be removed by fusion with nitre.

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